(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 611 743 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent: 02.07.1997 Bulletin 1997/27

(51) Int. Cl.[6]: C07C 2/30, C07C 11/02, C07C 11/107

(21) Application number: 94301097.5

(22) Date of filing: 16.02.1994

(54) **Process for producing alpha-olefin oligomer compositions**

Verfahren zur Herstellung von Zusammensetzungen von Oligemeren von Alpha-Olefinen

Procédé pour la production de compositions d'oligomères d'alpha-oléfines

(84) Designated Contracting States:
DE FR GB

(30) Priority: 17.02.1993 JP 28007/93
28.04.1993 JP 103084/93
20.10.1993 JP 286068/93

(43) Date of publication of application: 24.08.1994 Bulletin 1994/34

(60) Divisional application: 95116782.4

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EP-A- 0 608 447

Printed by Rank Xerox (UK) Business Services
2.14.8/3.4

Description

The present invention relates to a process for preparing α-olefin oligomers. More particularly, it relates to an industrially advantageous process of preparation of α-olefin oligomers in which it is possible to produce α-olefin oligomers principally composed of 1-hexene from ethylene with high selectivity and in a high yield.

Known oligomerization processes of α-olefins such as ethylene include methods which use a chromium-based catalyst composed of a specific chromium compound and a specific organoaluminium compound. For instance, JP-B-43 18707 discloses a process for producing 1-hexene from ethylene using a catalyst consisting of a chromium-containing VIA Group transition metal compound and a polyhydrocarbylaluminium oxide.

Also, JP-A-3-128904 (EP-A-416304) discloses a method for oligomerizing α-olefins using a catalyst obtained by reacting a chromium-containing compound having a chromium-pyrrolyl bond with an alkyl metal or a Lewis acid.

However, according to the process of JP-B-43-18707 (US-A-3347840), the amount of the by-product polyethylene which is produced with 1-hexene is large, and if the trimerization reaction is carried out under the conditions which decrease the yield of the by-product polyethylene, the catalyst activity is lowered.

Also, the method of JP-A-3-128904 (EP-A-416,304) has the problem that the activity of the catalyst is unsatisfactory, although the yield of the by-products such as polyethylene is lowered. Further, in this method, there are required, in addition to the α-olefin oligomerization process, a step for preparing a chromium-containing compound having at least a chromium-pyrrolyl bond from a chromium salt and metal pyrrolide, and a step for isolating said chromium-containing compound. Therefore not only does the oligomerization operation become too complicated but also the construction cost for the whole process is elevated. Moreover, it is very difficult to handle the chromium-containing compounds having at least a chromium-pyrrolyl bond since they are very unstable to air and to humidity.

The present invention seeks to provide a process for producing α-olefin oligomers such as 1-hexene with high selectivity and in a high yield without requiring any complicated operations.

The present invention also seeks to provide an industrially advantageous process for producing 1-hexene.

As a result of the present inventors' earnest studies in order to solve the above-mentioned problems, it has been found that by carrying out oligomerization of an α-olefin in a solvent by reacting the α-olefin in a chromium-based catalyst system comprising a combination of at least a chromium compound, an alkylaluminium compound and ammonia, an amine or a metal amide, in a contacting mode that the chromium compound and the alkylaluminium compound are not previously contacted with each other, α-olefin oligomers are obtained in a high yield. On the basis of this finding, the present invention has been attained.

Accordingly the present invention provides a process for preparing an α-olefin oligomer which comprises oligomerizing an α-olefin in a solvent in the presence of a chromium-based catalyst system comprising a combination of at least a chromium compound; ammonia, an amine or metal amide; and an alkylaluminium compound, in a contacting mode that the chromium compound and the alkylaluminium compound are not previously contacted with each other.

An α-olefin oligomer composition is obtainable from the process defined above which comprises not less than 85 % by weight of 1-hexene and not more than 15 % by weight of oligomers having not less than 10 carbon atoms and/or polymers.

In the present invention, the chromium-based catalyst comprises a combination of at least (a) a chromium compound, (b) ammonia, an amine or metal amide, and (c) an alkylaluminium compound.

The chromium compound is generally represented by the formula: CrX_n wherein X is an organic group, an inorganic group or an anionic atom; and n is an integer of 1 to 6. When n is not less than 2, each X may be the same or different. The valency of the chromium is 0 to 6. In the above formula n is preferably not less than 2.

The organic groups represented by X usually have 1 to 30 carbon atoms. Examples of such organic groups having 1 to 30 carbon atoms are a hydrocarbon group, carbonyl group, alkoxy group, carboxyl group, β-diketonate group, β-ketocarboxyl group, β-ketoester group and amide group. Examples of a hydrocarbon group having 1 to 30 carbon atoms are an alkyl, cycloalkyl, aryl, alkylaryl, aralkyl and cyclopentadienyl group. The inorganic group includes a chromium salt-forming group such as a nitrate group and sulfate group. The anionic (negative) atom includes oxygen and a halogen.

The preferred chromium compounds used in the present invention are chromium alkoxides, chromium carboxylates, chromium β-diketonates, salts of chromium with anions of β-ketoesters and chromium halides. Examples are chromium (IV) tert-butoxide, chromium (III) acetylacetonate, chromium (III) trifluoroacetylacetonate, chromium (III) hexafluoroacetylacetonate, chromium (III) (2,2,6,6-tetramethyl-3,5-heptanedionate), $Cr(PhCOCHCOPh)_3$ (wherein Ph represents phenyl group), chromium (II) acetate, chromium (III) acetate, chromium (III) 2-ethylhexanoate, chromium (III) benzoate, chromium (III) naphthenate, $Cr(CH_3COCHCOOCH_3)_3$, chromous chloride, chromic chloride, chromous bromide, chromic bromide, chromous iodide, chromic iodide, chromous fluoride and chromic fluoride.

Complexes composed of the above-mentioned chromium compounds and an electron donor can also be favorably used in the present invention. Examples of the electron donor are a nitrogen-containing compound, an oxygen-containing compound, a phosphorus-containing compound and a sulfur-containing compound.

The nitrogen-containing compound includes a nitrile, amine and amide. Examples are acetonitrile, pyridine,

dimethylpyridine, dimethylformamide, N-methylformamide, aniline, nitrobenzene, tetramethylethylenediamine, diethylamine, isopropylamine, hexamethyldisilazane and pyrrolidone.

The oxygen-containing compound includes an ester, ether, ketone, alcohol and aldehyde. Examples are ethyl acetate, methyl acetate, tetrahydrofuran, dioxane, diethyl ether, dimethoxyethane, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, acetone, methyl ethyl ketone, methanol, ethanol and acetaldehyde.

Examples of the phosphorus-containing compound are hexamethylphosphoramide, hexamethyl phosphorus triamide, triethyl phosphite, tributylphosphine oxide and triethylphosphine.

Examples of the sulfur-containing compound are carbon disulfide, dimethyl sulfoxide, tetramethylene sulfone, thiophene and dimethyl sulfide.

Thus, examples of a complexe composed of chromium compounds and an electron donor are ether complexes, ester complexes, ketone complexes, aldehyde complexes, alcohol complexes, amine complexes, nitrile complexes, phosphine complexes and thioether complexes of chromium halides. Preferred examples are $CrCl_3 \cdot 3THF$, $CrCl_3 \cdot 3dioxane$, $CrCl_3 \cdot (CH_3CO_2n\text{-}C_4H_9)$, $CrCl_3 \cdot (CH_3CO_2C_2H_5)$, $CrCl_3 \cdot 3(i\text{-}C_3H_7OH)$, $CrCl_3.3[CH_3(CH_2)_3CH(C_2H_5)CH_2OH]$, $CrCl_3 \cdot 3pyridine$, $CrCl_3 \cdot 2(i\text{-}C_3H_7NH_2)$, $[CrCl_3 \cdot 3CH_3CN] \cdot CH_3CN$, $CrCl_3 \cdot 3PPh_3$, $CrCl_2 \cdot 2THF$, $CrCl_2 \cdot 2pyridine$, $CrCl_2 \cdot 2[(C_2H_5)_2NH]$, $CrCl_2 \cdot 2CH_3CN$ and $CrCl_2 \cdot 2[P(CH_3)2Ph]$.

The chromium compound used in the present invention is preferably one which is soluble in hydrocarbon solvents. Examples are chromium β-diketonates, chromium carboxylates, salts of chromium with anions of β-ketoesters, chromium β-ketocarboxylates, chromium amide complexes, chromium carbonyl complexes, chromium carbene complexes, various kinds of cyclopentadienyl complexes of chromium, chromium alkyl complexes and chromium phenyl complexes. Specific examples are $Cr(CO)_6$, $(C_6H_6)Cr(CO)_3$, $(CO)_5Cr(=CCH_3(OCH_3))$, $(CO)_5Cr(=CC_6H_5(OCH_3))$, $CpCrCl_2$ (wherein Cp represents a cyclopentadienyl group), $(Cp^*CrClCH_3)_2$ (wherein Cp* represents a pentamethylcyclopentadienyl group) and $(CH_3)_2CrCl \cdot$

The chromium compound can be used in the form supported on a carrier such as an inorganic oxide, but it is preferably used in combination with other catalyst components without being supported on a carrier. In the present invention, the chromium-based catalyst is used in a specific contacting mode as described later. According to such a contacting mode, it is possible to obtain a high catalyst activity, even if the chromium compound is not supported on a carrier. When the chromium compound is used without supporting it on a carrier, it is possible to dispense with the complicated operations required for supporting the chromium compound on a carrier and to avoid the problem of an increase of the whole amount of catalyst used (the total amount of carrier and catalyst components) due to the use of a carrier.

The amine used in the present invention is generally a primary or secondary amine. Examples of the primary amine are ethylamine, isopropylamine, cyclohexylamine, benzylamine, aniline and naphthylamine. Examples of the secondary amine are diethylamine, diisopropylamine, dicyclohexylamine, dibenzylamine, bis(trimethylsilyl)amine, morpholine, imidazole, indoline, indol, pyrrole, 2,5-dimethylpyrrole, 3,4-dimethylpyrrole, 3,4-dichloropyrrole, 2,3,4,5-tetrachloropyrrole, 2-acylpyrrole, pyrazole and pyrrolidine.

The metal amide used in the present invention is generally one derived from ammonia or a primary or secondary amine. Specifically, an amide obtained from the reaction of ammonia or a primary or secondary amine and a metal of group IA, IIA, IIIB or IVB of the periodic table is usable. Examples of such metal amides are lithium amide, sodium ethylamide, calcium diethylamide, lithium diisopropylamide, potassium benzylamide, sodium bis(trimethylsilyl)amide, lithium indolide, sodium pyrrolide, potassium pyrrolide, potassium pyrrolidide, diethylaluminium pyrrolide, ethylaluminum dipyrrolide and aluminium tripyrrolide.

In the present invention, a secondary amine, a metal amide derived from a secondary amine or a mixture thereof is preferably used. Preferred examples of the secondary amines used in the present invention are pyrrole, 2,5-dimethylpyrrole, 3,4-dimethylpyrrole, 3,4-dichloropyrrole, 2,3,4,5-tetrachloropyrrole and 2-acylpyrrole. Preferred examples of the metal amides derived from the secondary amines are diethylaluminium pyrrolide, ethylaluminium dipyrrolide, aluminium tripyrrolide, sodium pyrrolide, lithium pyrrolide and potassium pyrrolide. Of the pyrrole derivatives, those having a hydrocarbon group in the pyrrole ring are especially preferred.

The alkylaluminium compounds used in the present invention are generally those represented by the formula (I):

$$R^1{}_mAl(OR^2)_nH_pX_q$$

wherein R^1 and R^2, which may be the same or different, are each a hydrocarbon group, usually having 1 to 15 carbon atoms, preferably 1 to 8 carbon atoms; X is a halogen atom; m, n, p and q are the numbers defined by $0<m\leq 3$, $0\leq n<3$, $0\leq p<3$ and $0\leq q<3$, respectively, and $m + n + p + q = 3$.

The above alkylaluminium compounds include the trialkylaluminium compounds of formula (2), the halogenated alkylaluminium compounds of formula (3), the alkoxyaluminium compounds of formula (4) and the alkylaluminium hydride compounds of formula (5):

$$R^1{}_3Al \qquad (2)$$

$$R^1_mAlX_{3-m}\ (1.5 \le m < 3) \tag{3}$$

$$R^1_mAl\,(OR^2)_{3-m} \tag{4}$$

($0<m<3$, preferably $1.5 \le m<3$)

$$R^1_mAlH_{3-m} \tag{5}$$

($0<m<3$, preferably $1.5 \le m<3$)

Examples of said alkylaluminium compounds are trimethylaluminium, triethylaluminium, triisobutylaluminium, diethylaluminium monochloride, diethylaluminium ethoxide and diethylaluminium hydride. Of these compounds, trialkylaluminium is especially preferred because of minimized formation of by-product polymers.

In the present invention, oligomerization of an α-olefin is carried out in a solvent using a catalyst composed of said catalytic components. It is indispensable to conduct oligomerization of an α-olefin by reacting the said α-olefin in a chromium-based catalyst system in a contacting mode such that the chromium compound and the alkylaluminium compound are not previously contacted with each other. Due to such a specific contacting mode, a trimerization reaction is allowed to take place selectively, enabling a high production yield of 1-hexene from ethylene as the starting material.

The specific contacting mode can be effected by various methods such as those mentioned below (the term "ammonia, an amine or metal amide" is represented by "amine"):

(1) an α-olefin and a chromium compound are introduced into a solution containing an amine and an alkylaluminium compound (contacting method A);
(2) an a-olefin and an alkylaluminium compound are introduced into a solution containing a chromium compound and an amine (contacting method B);
(3) an α-olefin, an amine and an alkylaluminium compound are introduced into a solution containing a chromium compound (contacting method C);
(4) an α-olefin, a chromium compound and an amine are introduced into a solution containing an alkylaluminium compound (contacting method D);
(5) a chromium compound, an amine, an alkylaluminium compound and an α-olefin are introduced into a reactor simultaneously and separately (contacting method E).

In the present invention, the expression "in a contacting mode that the chromium compound and the alkylaluminium compound are not previously contacted with each other" means that the contact of said two components is not allowed until the oligomerization reaction takes place. Furthermore this contacting mode is performed when introducing the α-olefin and each component of the chromium-based catalyst into the reactor.

Each solution used in the above-described contacting methods is prepared using a reaction solvent. In the present invention, the amount of a chromium compound is usually 1.0×10^{-7} to 0.5 mol, preferably 1.0×10^{-6} to 0.2 mol, more preferably 1.0×10^{-5} to 0.05 mol based on one litre of solvent. The amount of the alkylaluminium compound is usually not less than 50 mmol, preferably, not less than 0.1 mol based on one mol of chromium compound in view of catalyst activity and trimer selectivity. The upper limit of the alkylaluminium compound is preferably 1.0×10^4 mol based on one mol of chromium compound. Ammonia, an amine or metal amide is used in an amount of usually not less than 0.001 mol, preferably 0.005 to 1,000 mol, more preferably 0.01 to 100 mol based on one mol of chromium compound.

In the present invention, the molar ratio of (a) the chromium compound, (b) the ammonia, amine or metal amide, and (c) the alkylaluminium compound is preferably adjusted so that (a) : (b) : (c) = 1 : 2 to 4 : 4 to 8, more preferably 1 : 2.5 to 3.5 : 4.5 to 6.5. By combining such specific conditions of molar ratio and reaction temperature (not more than 70°C), it is possible to produce α-olefin oligomers, for example hexenes, in a yield of not less than 85 % by weight, preferably 90 % by weight (relative to the total amount of products), and further, the selectivity of 1-hexene in the produced hexenes can be enhanced to 99% or more.

The reason why the activity of the oligomerization reaction of an α-olefin is lowered when a chromium-based catalyst is used in a contacting mode that the chromium compound and the alkylaluminium compound are allowed to contact with each other before taking place the oligomerization, is not yet clarified, but it may be accounted for as follows:

It is considered that when the chromium compound and the alkylaluminium compound are contacted with each other, there takes place a ligand exchange reaction between the ligand coordinating to the chromium compound and the alkyl group in the alkylaluminium compound. The alkyl-chromium compound produced from such a reaction is per se unstable, which is unlike alkyl-chromium compounds obtained in ordinary ways. Therefore, the reduction and decomposition reaction of the alkyl-chromium compound preferentially proceeds, and consequently there is induced a demetallization improper to the α-olefin oligomerization reaction. This results in a lowering of the α-olefin oligomerization reaction activity.

In the present invention, by jointly using as additive components: (d) a non-coordinating Lewis acid-containing com-

pound, (e) a non-conjugated diene compound, or (f) an aromatic hydrocarbon compound which may have an aliphatic hydrocarbon substituent, it is possible to enhance the selectivity (purity) of the produced α-olefin and the catalyst activity, and to produce an α-olefin oligomer such as 1-hexene with high selectivity, without restricting the molar ratio of the chromium compound, the ammonia, amine or metal amide, and the alkylaluminium compound as specified above. The reason is not yet clarified, but this may be accounted for as follows:

As a non-conjugated diene coordinates to the chromium-based catalyst composed of a chromium compound, ammonia, an amine or metal amide, and an alkylaluminium compound, generation of position isomers due to double bonds contained in the hexene is suppressed, so that the purity of 1-hexene is elevated. It is considered that the same result is obtained with the aromatic hydrocarbon compound which may have an aliphatic hydrocarbon substituent. Also, coordination of a non-conjugated diene to the chromium atom increases the electron density on the chromium atom, resulting in an enhancement of the oligomerization reaction activity of the electron-enriched chromium catalyst itself. In the case of the aromatic hydrocarbon compound having not less than three aliphatic hydrocarbon substituents, the coordinating ability for the chromium catalyst is increased since the electron density on the aromatic ring is raised, and consequently the oligomerization reaction activity of the electron-enriched chromium catalyst itself is enhanced.

On the other hand, it is supposed that the non-coordinating Lewis acid-containing compound contributes to the activation of the active species of the chromium-based catalyst or its precursor. When using a non-coordinating Lewis acid-containing compound it is possible to produce α-olefin oligomers mainly composed of 1-hexene from ethylene with high selectivity and in a high yield. Said compounds used as additional components may be added to the reaction system in whatever manner.

Examples of the non-conjugated diene compound are chain non-conjugated dienes such as 1,5-hexadiene, 2,5-hexadiene, 1,6-diphenyl-2,5-hexadiene, 1,6-heptadiene, 2,5-heptadiene, 1,5-octadiene, 2,6-octadiene and 1,7-octadiene, and cyclic non-conjugated dienes such as 1,5-cyclooctadiene, norbornadiene, dicyclopentadiene, 4-vinylcyclohexene, hexamethylbicyclo[2,2,0]hexadiene, 1,4-cyclohexadiene and 1,4-cycloheptadiene. These dienes may have an aliphatic or aromatic hydrocarbon group such as an alkyl, aralkyl or aryl group as a substituent. It is preferred to use a non-conjugated diene having not more than 20 carbon atoms. In view of the potent ability of coordination to the chromium atom, it is preferred to use a cyclic non-conjugated diene.

The amount of the non-conjugated diene compound used in the reaction of the present invention is not restricted in its upper limit provided that it is not less than 0.1 ppm, preferably not less than 10 ppm, based on the amount of the charged solutions (the total amount of a solvent and non-conjugated diene compound). The non-conjugated diene compound may be used as a solvent, but preferably it is used in an amount of 0.1 to 20 % by volume based on the amount of the charged solutions.

The aromatic hydrocarbon compounds having aliphatic hydrocarbon substituents are preferably divided into aromatic hydrocarbon compounds having not less than three aliphatic hydrocarbon substituents and aromatic hydrocarbon compounds having not more than two aliphatic hydrocarbon substituents. Examples of aliphatic hydrocarbon substituents are chain or alicyclic hydrocarbon groups such as methyl, ethyl, propyl, isopropyl, butyl, cyclopropyl, cyclobutyl and cyclohexyl.

Examples of aromatic hydrocarbon compounds having not less than three aliphatic hydrocarbon substituents are 1,3,5-trimethylbenzene(mesitylene), 1,2,4-trimethylbenzene, 1,3,5-triethylbenzene, hexamethylbenzene, 1,3,5-triisopropylbenzene, 1,3,5-tri-t-butylbenzene, 1,2,4,5-tetramethylbenzene and 1,2,4,5-tetramethylnaphthalene.

The amount of the aromatic hydrocarbon compound having not less than three aliphatic hydrocarbon substituents used in the reaction of the present invention is not restricted in its upper limit, provided that it is not less than 0.1 ppm, preferably not less than 10 ppm, based on the amount of the charged solutions (the total amount of a solvent and an aromatic hydrocarbon compound). Such an aromatic hydrocarbon compound may be used as a solvent, but preferably it is used in an amount of 0.1 to 95 % by volume based on the amount of the charged solutions.

Examples of the aromatic hydrocarbon compound having not more than two aliphatic hydrocarbon substituents are benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, cumene, p-cymene, 1,4-dibutylbenzene, tert-butylbenzene, 1,4-di-tert-butylbenzene, cyclohexylbenzene, 1,4-dicyclohexylbenzene, methylnaphthalene, 2,6-dimethylnaphthalene and 1,5-dimethylnaphthalene.

The amount of the aromatic hydrocarbon compound having not more than two aliphatic hydrocarbon substituents used in the reaction of the present invention is not restricted in its upper limit, provided that it is not less than 0.1 ppm, preferably not less than 10 ppm, based on the amount of the charged solutions (the total amount of a solvent and an aromatic hydrocarbon compound). Such an aromatic hydrocarbon compound may be used as a solvent, but preferably it is used in an amount of 0.1 to 95 % by volume, preferably 0.5 to 40 % by volume, based on the amount of the charged solutions.

The non-coordinating Lewis acid-containing compounds used in the present invention are represented by formula (6) or (7):

$$[L]^{+}\left[\begin{array}{c} R^{1} \\ | \\ R^{4}-M^{1}-R^{2} \\ | \\ R^{3} \end{array}\right]^{-} \qquad (6)$$

$$\begin{array}{c} R^{5} \\ | \\ R^{7}-M^{2}-R^{6} \end{array} \qquad (7)$$

wherein M^1 and M^2 are each an element selected from groups IIIB, IVB, VB and VIB of the periodic table, preferably B, Al or In; and R^1 to R^7 are each independently an organic group, an inorganic group of an anionic atom, such as a hydrogen atom, dialkylamino group, alkoxy group having 1 to 20 carbon atoms, aryloxy group having 6 to 20 carbon atoms, alkyl group having 1 to 20 carbon atoms, aryl group having 6 to 20 carbon atoms, alkylaryl group having 7 to 20 carbon atoms, arylalkyl group having 7 to 20 carbon atoms, halogen-substituted hydrocarbon group having 1 to 20 carbon atoms, acyloxy group having 1 to 20 carbon atoms, alkoxyaryl group having 7 to 20 carbon atoms, halogen-substituted alkoxyaryl group having 7 to 20 carbon atoms, organic metalloid group, nitrate group or halogen atom. Two or more of these groups and/or atoms may be combined to form a ring.

Examples of R^1 to R^7 are a dimethylamino group, diethylamino group, pyrrolyl group, 2,5-dimethylpyrrolyl group, methoxy group, ethoxy group, isopropoxy group, n-butoxy group, t-butoxy group, phenoxy group, 2,6-dimethylphenoxy group, 2,6-t-butylphenoxy group, naphthylphenoxy group, methyl group, ethyl group, n-propyl group, n-butyl group, n-octyl group, phenyl group, 3-methylphenyl group, 2,4-dimethylphenyl group, 2,6-dimethylphenyl group, 3,5-dimethylphenyl group, 2,3-dimethylphenyl group, 2,4,6-trimethylphenyl group, 2,3,5-trimethylphenyl group, 2,3,4-trimethylphenyl group, 3-t-butylphenyl group, 2,6-di-t-butylphenyl group, benzyl group, p-fluorophenyl group, 3,5-difluorophenyl group, pentachlorophenyl group, 3,4,5-trifluorophenyl group, pentafluorophenyl group, 3,5-di(trifluoromethyl)phenyl group, 3-methoxyphenyl group, 2,4-dimethoxyphenyl group, 2,6-dimethoxyphenyl group, 3,5-dimethoxyphenyl group, 2,3-dimethoxyphenyl group, 2,4,6-trimethoxyphenyl group, 2,3,5-trimethoxyphenyl group, 2,3,4-trimethoxyphenyl group, 3,5-bis(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)phenyl group, 3-(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl-5-(trifluoromethyl)phenyl group, 3-(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenyl group, 3,5-bis(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy))-1-(trifluoromethyl)ethyl)phenyl group, trimethylsilyl group, trimethylgermyl group, diphenylarsine group, dicyclohexylantimony group, pentafluorotelluroxy group, F, Cl, Br and I.

$[L]^+$ in formula (6) is a cation containing an element selected from groups IA, VIIA, VIII, IB and IIIB to VIB of the periodic table. L is represented by M^3, $M^4R^8R^9$, $E^1R^{10}R^{11}R^{12}$ or $E^2R^{13}R^{14}R^{15}R^{16}$, wherein M^3 is an element selected from groups IA, IB and IIB Groups of the periodic table, M^4 is an element selected from the groups VIIA and VIII of the periodic table, E^1 is carbon atoms, an oxygen atom or sulfur atom, and E^2 is a nitrogen atom or phosphorus atom.

M^3 is preferably Li, Na, K or Ag, and M^1 is preferably Mn, Fe, Co or Ni.

R^8 and R^9 are each substituents selected from a cyclopentadienyl group, substituted cyclopentadienyl group, indenyl group and fluorenyl group. R^8 and R^9 may be combined to form a ring. The substituent of the substituted cyclopentadienyl group of R^8 and R^9 is usually an alkyl group having 1 to 6 carbon atoms, and the number of substituents is an integer of 1 to 5. Examples of substituted cyclopentadienyl groups are methylcyclopentadienyl, n-butylcyclopentadienyl and pentamethylcyclopentadienyl.

R^{10} to R^{16} are each a subtituent selected from a hydrogen atom, halogen atom, alkyl group having 1 to 20 carbon atoms, aryl group having 6 to 20 carbon atoms, alkylaryl group having 7 to 20 carbon atoms, arylalkyl group having 7 to 20 carbon atoms or organic metalloid group. Examples of R^{10} to R^{16} are a hydrogen atom, methyl group, ethyl group, n-propyl group, n-butyl group, n-octyl group, cyclohexyl group, phenyl group, benzyl group, 3-methylphenyl group, 2,4-dimethylphenyl group, 2,6-dimethylphenyl group, 3,5-dimethylphenyl group, 2,3-dimethylphenyl group, 2,4,6-trimethylphenyl group, 2,3,5-trimethylphenyl group , 2,3,4-trimethylphenyl group, 3-t-butylphenyl group, 2,6-di-t-butylphenyl group, F, Cl, Br and I.

In the compounds of formula (6) or (7) those in which M^1 or M^2 is boron are preferred.

Of the compounds of formula (6), the following compounds are especially preferred:

As compounds wherein L is M^3, silver tetraphenylborate, sodium tetraphenylborate, silver tetrakis(pentafluorophenyl)borate, lithium tetrakis(pentafluorophenyl)borate, silver tetrakis(pentafluorotelluroxy)borate, silver tetrafluoroborate, silver tetrafluoroarsenate and silver tetrafluoroantimonate.

As compounds wherein L is $M^4R^8R^9$, ferrocenium tetraphenylborate, manganese tetraphenylborate (tetraphenyl-

porphyrin), ferrocenium tetrakis(pentafluorophenyl)borate, decamethylferrocenium tetrakis(pentafluorophenyl)borate, acetylferrocenium tetrakis(pentafluorophenyl)borate, formylferrocenium tetrakis(pentafluorophenyl)borate and cyanoferrocenium tetrakis(pentafluorophenyl)borate.

As compounds wherein L is $E^1R^{10}R^{11}R^{12}$, trityl tetraphenylborate, trityl tetrakis(pentafluorophenyl)borate, trimethylsulfonium tetraphenylborate, benzyldimethylsulfonium tetraphenylborate and benzyldimethylsulfonium tetrakis(pentafluorophenyl)borate.

As compounds wherein L is $E^2R^{13}R^{14}R^{15}R^{16}$, ammonium tetraphenylborate, triethylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, trimethylammonium tetraphenylborate, pyrrolium tetraphenylborate, 2,5-dimethylpyrrolium tetraphenylborate, ammonium tetrakis(pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(pentafluorophenyl)borate, anilinium tetrakis(pentafluorophenyl)borate, monomethylanilinium tetrakis(pentafluorophenyl)borate, dimethylanilinium tetrakis(pentafluorophenyl)borate, tetraphenylphosphonium tetrakis(pentafluorophenyl)borate, tetrabutylammonium tetrakis(pentafluorophenyl)borate, methyldiphenylammonium tetrakis(pentafluorophenyl)borate, triphenylammonium tetrakis(pentafluorophenyl)borate, pyridinium tetrakis(pentafluorophenyl)borate, dimethyl(m-nitroanilinium) tetrakis(pentafluorophenyl)borate, dimethyl(p-bromoanilinium) tetrakis(pentafluorophenyl)borate, (p-cyanopyridinium) tetrakis(pentafluorophenyl)borate, trimethylanilinium tetrakis(pentafluorophenyl)borate, (N-methylpyridinium) tetrakis(pentafluorophenyl)borate, trimethylsulfinium tetrakis(pentafluorophenyl)borate, (o-cyano-N-methylpyridinium) tetrakis(pentafluorophenyl)borate, dimethyldiphenylammonium tetrakis(pentafluorophenyl)borate, (p-cyano-N-benzylpyridinium) tetrakis(pentafluorophenyl)borate, methyltriphenylammonium tetrakis(pentafluorophenyl)borate, pyrrolium tetrakis(pentafluorophenyl)borate, 2,5-dimethylpyrrolium tetrakis(pentafluorophenyl)borate, dimethylanilinium tetrakis(3,5-di(trifluoromethyl)phenyl)borate, triethylammonium hexafluoroarsenate, dimethylanilinium tetrakis(3,5-bis(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl))phenylborate, dimethylanilinium tetrakis(3-(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenylborate, dimethylanilinium tetrakis(3-(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl))phenylborate, dimethylanilinium tetrakis(3,5-bis(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)phenylborate, tetraethylammonium tetraphenylborate, methyltri(n-butyl)ammonium tetraphenylborate, benzyltri(n-butyl)ammonium tetraphenylborate, trimethylanilinium tetraphenylborate, dimethyldiphenylammonium tetraphenylborate, methyltriphenylammonium tetraphenylborate, methylpyridinium tetraphenylborate, benzylpyridinium tetraphenylborate, methyl(2-cyanopyridinium) tetraphenylborate, tetraethylammonium tetrakis(pentafluorophenyl)borate, methyltri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, benzyltri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, methyl(4-cyanopyridinium) tetrakis(pentafluorophenyl)borate and benzylpyridinium tetrakis(pentafluorophenyl)borate.

Preferred compounds of formula (7) are tris(pentafluorophenyl)boron, tris(3,5-bis(1-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)phenylboron, tris-3-methoxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl)phenylboron, tris(3-(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)-5-(trifluoromethyl))phenylboron, tris(3,5-bis(2,2,2-trifluoro-1-(2,2,2-trifluoro-1-(2,2,2-trifluoroethoxy)-1-(trifluoromethyl)ethyl)phenylboron, triphenylboron and tris(pentafluorotelluroxy)boron.

A non-coordinating Lewis acid-containing compound is usually used in an amount of not less than 0.001 mol, preferably 0.005 to 1,000 mol, more preferably 0.01 to 100 mol, based on one mol of the chromium compound.

As the α-olefin used as starting material in the present invention, substituted or non-substituted α-olefins having 2 to 30 carbon atoms are usable. Examples of α-olefins are ethylene, propylene, 1-butene, 1-hexene, 1-octene, 3-methyl-1-butene and 4-methyl-1-pentene. Ethylene is especially preferred since it is possible to produce 1-hexene as a trimer with a high selectivity and in a high yield.

As the solvent used in the reaction of the present invention, there can be used chain or alicyclic saturated hydrocarbons having 1 to 20 carbon atoms such as butane, pentane, 3-methylpentane, hexane, heptane, 2-methylhexane, octane, cyclohexane, methylcyclohexane and decalin; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, mesitylene and tetralin; chain chlorinated hydrocarbons such as chloroform, carbon tetrachloride, methylene chloride, dichloroethane, trichloroethane and tetrachloroethane; and chlorinated aromatic hydrocarbons such as chlorobenzene and dichlorobenzene. These solvents may be used either singly or as a mixture. The α-olefin used as the starting material for the reaction or the α-olefins other than the main starting material for the reaction can also be used as solvent. An α-olefin having 4 to 30 carbon atoms, especially an α-olefin which is liquid at room temperature, is preferred as a solvent. As a general solvent, an open chain saturated hydrocarbon having not more than 7 carbon atoms, preferably 4 to 7 carbon atoms, is preferably used. Alicyclic saturated hydrocarbons are also preferred. Use of a solvent such as mentioned above proves helpful for suppressing formation of the by-product polymers. A high catalytic activity can be obtained by using an alicyclic hydrocarbon. Examples of the saturated hydrocarbons having not more than 7 carbon atoms are propane, butane, pentane, hexane and heptane. These solvents may have a branched chain structure.

The reaction temperature is usually 0 to 250°C, preferably 10 to 150°C, more preferably 25 to 70 °C. The reaction pressure can be suitably selected from between ordinary pressure and 2.4×10^7 Pa (250 kg/cm^2), but usually a pressure between ordinary pressure and 9.8×10^6 Pa (100 kg/cm^2) is sufficient. The reaction time is usually one minute to

20 hours, preferably 0.5 to 6 hours. The type of reaction may be batchwise, semi-batchwise or continuous. The presence of hydrogen in the reaction system is preferable since the catalytic activity is enhanced as well as the selectivity of the objective trimer. The pressure of the co-existent hydrogen is usually 9.8×10^3 to 9.8×10^6 Pa (0.1 to 100 kg/cm^2), preferably 9.8×10^4 to $78{,}4 \times 10^4$ Pa (1 to 80 kg/cm^2).

For a continuous reaction, said specific contact can be performed in the different zones. In this case, a pipe reactor or a one-stage or multi-stage mixing tank is used as a reaction vessel. A pipe reactor is a reaction apparatus comprising a straight pipe, a coiled or U-shaped curved pipe designed such that the reactants are introduced from one end thereof and the reaction product is discharged from the other end. A multi-stage mixing tank is a reaction apparatus in which, basically, the reactants are introduced initially into the first of the plural sets of mixing tanks arranged in series to each other, the introduced reactants being transferred into the ensuing tanks successively, and the reaction product is discharged out from the final tank.

In the present invention, when using a pipe reactor, part of the reactants are introduced in a front portion (end) of the straight or curved pipe, and the rest of the reactants are introduced in a back point (portion) of the introducing portion of a part of the reactants and in the first half thereof. For instance, ammonia, an amine or metal amide, and an alkylaluminium compound are introduced in the front end of the pipe reactor and an α-olefin and a chromium compound are introduced in a back portion of the introducing portion of the ammonia, amine or metal amide, and the alkylaluminium compound. Alternatively, a chromium compound, and ammonia, an amine or metal amide may be introduced from the front end of the pipe reactor, and an α-olefin and an alkylaluminium compound are introduced in a back portion of the introducing portion of the chromium compound, and the ammonia, amine or metal amide. In a pipe reactor any number of reactant introducing points may be provided so long as the α-olefin and a chromium-based catalyst are contacted with each other in a contacting mode such that the chromium compound and the alkylaluminium compound are not previously contacted with each other.

When using a multi-stage mixing tank assembly in the present invention, for example, ammonia, an amine or metal amide, and an alkylaluminium compound are introduced into the first tank, and an α-olefin and a chromium compound are introduced into the second tank. Also, a chromium compound and ammonia, an amine or metal amide may be introduced into the first tank, and an α-olefin and an alkylaluminium compound are introduced into the second tank. In this case, there may be provided any desired number of mixing tanks so long as an α-olefin and a chromium-based catalyst are contacted with each other in a contacting mode such that the chromium compound and the alkylaluminium compound are not contacted with each other.

In the present invention, an antistatic agent inert to the catalyst components is allowed to exist in the reaction mixture to prevent deposition of the by-product polymer to the reactor, distillation column, other incidental equipment and piping. The "antistatic agent inert to the catalyst components" is an antistatic agent whose presence in the reaction system does not affect the activity of said chromium-based catalyst. As such an antistatic agent, those already proposed in the field of polymerization of α-olefins can be used in the present invention. For example, the antistatic agents disclosed in JP-B-50 38158 (US-A-3 919 185), namely polyvalent metal salts of organic acids having a molecular weight of at least 300, more specifically, for example, polyvalent metal alkylsalicylates and polyvalent metal sulfonated dialkyl aliphatic dicarboxylates can be used. The alkyl group of the alkylsalicyclic acids is specifically one having 14 to 18 carbon atoms. The polyvalent metals usable include magnesium, copper, zinc, cadminum, aluminium, lead, chromium, molybdenum and manganese. The polyvalent metal salts may be used either singly or as a mixture. They may also be used as an admixture with a high polymeric electrolyte.

Examples of the high polymeric electrolytes usable in the present invention are stearyl methacrylate/methacrylic acid copolymer, β-hydroxyethyl methacrylate/stearyl methacrylate/ methacrylic acid copolymer, ethyleneimine polymers, 2-methyl-5-vinylpyridine polymers, copolymer of 2-methyl-5-vinylpyridine and mixture of lauryl methacrylate and stearyl methacrylate and lauryl methacrylate/stearyl methacrylate/methyl methacrylate/2-methyl-5-vinylpyridine polymer. A copolymer of 2-methyl-5-vinylpyridine and lauryl methacrylate (number of carbon atoms in the alkyl group: 16-18) is especially preferred.

"ASA-3" (produced by Shell Chemical Co.) as an antistatic agent can be favorably used in the present invention. This commercial product is an antistatic agent comprising about 20 wt% of chromium (III) alkylsalicylates having 14 to 18 carbon atoms, about 10 wt% of the calcium salt of di-2-ethylhexyl sulfosuccinate, about 45 wt% of a copolymer of 2-methyl-5-vinylpyridine and the C_{17} alkyl ester of methacrylic acid (high polymeric electrolyte) and about 25 wt% of m-xylene.

Another example of an antistatic agent usable in the present invention is disclosed in JP-B-56-51164 (US-A-4 182 810) which is a composition containing (i) a polysulfone copolymer of sulfur dioxide and an olefin-based compound, (ii) a polymer-like polyamine which is the reaction product of epichlorohydrin and aliphatic primary monoamine or N-aliphatic hydrocarbylalkylenediamine and (iii) an oil-soluble sulfonic acid. Examples of the oil-soluble sulfonic acid are alkanesulfonic acid and petroleum sulfonic acid. This composition preferably contains a solvent selected from benzene, toluene, xylene, cyclohexane, fuel oil, isobutane and a mixture thereof. It is stated that the composition contains (i) 5-25 wt% polysulfone copolymer, (ii) 5-25 wt% polymer-like polyamine, (iii) 5-30 wt% oil-soluble sulfonic acid, and 20-85 wt% solvent.

"Stadis 450" and "Stadis 425" (produced by E.I. Du Pont de Nemours & Co.) as antistatic agents can be favorably used as an antistatic agent in the present invention. "Stadis 450" is a composition comprising about 14 wt% of polybutene sulfate, about 3 wt% of aminoethanolepichlorohydrin polymer, about 13 wt% of alkylbenzenesulfonic acid, about 70 wt% of toluene and trace amounts of a quaternary ammonium salt of an aliphatic alkyl and propyl alcohol. "Stadis 425" is a composition comprising 2 to 7 wt% of polyaminopolyol, 2 to 8 wt% of dodecylbenzenesulfonic acid, 60 to 70 wt% of kerosine, 10 to 20 wt% of toluene, less than 0.017 wt% of benzene and 2 to 7 wt% of mixed aromatic solvent (C_{9-17}).

Other antistatic agents are disclosed in JP-B-63-66321 (EP-A-107127), that is, (I) higher fatty acid soaps of formula: RCOOM (wherein R is a C_{12-22} saturated or unsaturated hydrocarbon group; and M is an alkali or alkaline earth metal); (II) sulfuric acid esters of higher alcohols of formula: $ROSO_3M$ (wherein R and M are as defined above), sulfuric acid esters of secondary higher alcohols of formula: $R(R)CHOSO_3M$ (wherein R and M are as defined above); (III) alkali or alkaline earth metal salts of the reaction product of, for example, castor oil, olive oil, peanut oil or cottonseed oil and sulfuric acid; (IV) alkali or alkaline earth metal salts of compounds of polyhydric alcohols and higher fatty acids in which the residual OH groups have been turned into sulfuric acid esters with the partial esters of said polyhydric alcohols and higher fatty acids; (V) sulfuric acid ester salts of higher fatty acid alkylolamides of formula: $RCONH(CH_2)_n$ (wherein R and M are as defined above; and n is an integer of 1 to 10); (VI) compounds of formula: $R(OCH_2CH_2)_nOSO_3$ (wherein R, M and n are as defined above); (VII) higher alkyl sulfonates of formula: RSO_3M (wherein R and M are as defined above); (VIII) alkylallyl sulfonates; (IX) condensates of compounds of formula: RCOCl and compounds of formula: $RNH(CH_2)_nSO_5M$ (wherein R, M and n are as defined above); (X) condensates of compounds of formula: RCOCl and compounds of formula: $HO(CH_2)_nSO_3M$ (wherein R, M and n are as defined above); (XI) alkali or alkaline earth metal salts of dialkylsulfosuccinic acid; and (XII) alkali or alkaline earth metal salts of partial esters of higher alcohols and phosphoric acid. Among these antistatic agents, alkaline metal salts of dialkylsulfosuccinic acid are preferred.

An antistatic agent is introduced into the reactor along with the starting material α-olefin, catalyst components and solvent, or it is mixed with these components and then introduced into the reactor. When the reaction is carried out batchwise, the antistatic agent may be added into the reaction mixture composed of the above-mentioned components in a relatively early phase of the reaction. The concentration of the antistatic agent in the reaction mixture is usually 0.003 to 30 mg/l, preferably 0.01 to 2 mg/l, based on one litre of the reaction mixture.

In the present invention, it is preferred that the oligomerization of an α-olefin is carried out at a temperature of 25 to 70°C using a saturated hydrocarbon having not more than 7 carbon atoms as a solvent. This process allows easy separation of the by-product polymers. That is, when the reaction is conducted under the above conditions, the by-product polymers take a granular form and can be easily separated.

The by-product polymers in the reaction mixture are separated out without allowing them to melt. The granular by-product polymers can be very easily separated out as compared with conventional polymer separation. Further, the granular by-product polymers are scarcely deposited on the inner wall of the piping, so that it is possible to avoid such problems as blocking of the piping and reduction of the heat transfer coefficient. If the reaction mixture is stirred to disperse the by-product polymers prior to their separation, it is possible to control the grain size of the granular by-product polymers.

Stirring of the reaction mixture can be conducted by any suitable means, for example a rotary blade stirrer, a blow stirrer using an inert gas or a circulation pump system, but usually a rotary blade stirrer is employed. The shape of the blade in the rotary blade stirrer may be suitably selected from various known types such as the turbine type, fan turbine type, curved blade fan turbine type, propeller type, simple paddle type (flat blade type), gate type and shutter type. If necessary, a baffle plate may also be used along with a rotary blade stirrer.

When a rotary blade stirrer is used, the grain size of the granular by-product polymers differs according to the stirring speed (shearing force), that is, the grain size becomes small when the stirring speed is increased, while the grain size is enlarged when the stirring speed is lowered. Usually the preferred grain size of the granular by-product polymers is 100 to 3,000 μm, more preferably 300 to 1,000 μm. Therefore, the stirring speed (shearing force) of the rotary blade stirrer is preferably selected such that the grain size of the granular by-product polymers falls within the above-mentioned range.

The specific stirring speed differs depending on the factors relating to stirring element, such as the shape of the blade, blade length, blade width, slat angle, number of slats and slat mounting height, the factors relating to the oligomerization reactor, such as the diameter of oligomerization reactor (autoclave), depth of reaction mixture, width of baffle plate and number of baffle plates used, and the factors relating to the reaction mixture, such as the density and viscosity, so that it is necessary to determine the appropriate stirring speed by a conducting a model test before carrying out the oligomerization reaction. In the case of a one-stage simple paddle type (flat blade type) stirrer, the grain size of the granular by-product polymers can generally be controlled to fall within the range of 100 to 3,000 μm by adjusting the stirring speed to 200 to 1,000 r.p.m.

Separation of the by-product polymers can be accomplished using a known solid/liquid separator. In the present invention, a filter or a centrifuge is preferably used. Separation of the granular by-product polymers can be accomplished with surprising easiness by using a solid/liquid separator of a structure in which the solid matter is separated by

centrifugation while discharging the separated solid matter out of the system by a rotary screw.

A solid/liquid separator of the above-described specific structure is per se known. For example, this type of separator is commercially available under the trade name "Sharples Super Decanter" (manufactured by Tomoe Kogyo Co., Ltd.). Also, various types of screw-adapted centrifuges are marketed by Ishikawajima Harima Industrial Co., Ltd.

Said solid/liquid separator is mainly composed of an external bowl having a shape of a cylinder and a cone combined integrally with each other, said bowl being supported at its both ends by bearings and provided with a discharge port for separating liquid and solid matter, an internal screw disposed inside said bowl coaxially therewith, and having provided therearound a screw blade and a plurality of liquid spouts in the body portion, a feed pipe for feeding the stock solution through the liquid spouts in the body portion of said internal screw, a rotatory mechanism (planetary gears) designed to produce a rotational difference between said external bowl and internal screw in the same direction, and a casing enclosing said external bowl, and having a discharge port for separating liquid and solid matter. There are two types of separator, such as a vertical separator and horizontal separator.

In operation of the above solid/liquid separator, the external bowl is rotated at a high speed while the internal screw is rotated at a lower speed, whereby the stock solution supplied from the feed pipe is centrifuged, with the solid matter being separated to the wall surface side of said bowl and discharged out of the system by the conveying action of the screw. In the present invention, the operating conditions of said solid/liquid separator are not subjected to any specific restrictions, but usually the external bowl is operated at a speed of 2,000 to 6,000 r.p.m., while the internal screw is operated at a speed of about 500 to 1,000 r.p.m. lower than the speed of the external bowl.

The α-olefin oligomers yielded after separation of the by-product polymers in the reaction mixture are purified, if necessary. Usually distillation is employed for purification, and this allows recovery of the objective substance with a high purity.

In the present invention, part of the α-olefin oligomers obtained may be converted into a saturated hydrocarbon by hydrogenation and the saturated hydrocarbon may be recycled to the oligomerization reaction system to realize a significant reduction of solvent cost. The fraction of the α-olefin oligomers to be subjected to the hydrogenation treatment is not specifically defined, but it is preferred to separate the product into a fraction with 4 to 6 carbon atoms and a fraction with not less than 8 carbon atoms by distillation and to subject the fraction with not less than 8 carbon atoms to the hydrogenation treatment.

The amount of the α-olefin oligomers to be subjected to hydrogenation may be such as equivalent to the amount lost in the steps of oligomerization reaction, separation of the by-product polymers and distillation. When the α-olefin oligomers with not less than 8 carbon atoms are subjected to the hydrogenation treatment according to said preferred operation mode, since the yield of the α-olefin oligomers with not less than 8 carbon atoms is relatively small in the oligomerization reaction of the present invention, it is possible to obtain a saturated hydrocabon in an amount equivalent to the loss of the reaction solvent if all said α-olefin oligomers are subjected to the hydrogenation treatment.

Thus, hydrogenation of the α-olefin oligomers is performed to convert the α-olefin contained in said oligomers into a saturated hydrocabon. To perform such a hydrogenation, the generally know hydrogenation treatment conditions can be employed. For example, the α-olefin oligomers are subjected to a hydrogenation treatment using a platinum catalyst supported on γ-alumina at a temperature of 30 to 150°C under a pressure of 9.8×10^5 to 68.6×10^5 Pa (10 to 70 kg/cm^2). However, the hydrogenation treatment conditions usable in the present invention are not limited to those described above.

Other fractions of α-olefin oligomers, for example one with 4 to 6 carbon atoms, are further purified by distillation and recovered as a high-purity objective product. In the present invention, particularly high-purity 1-hexene can be produced from ethylene in an industrially advantageous way.

In the present invention, the distillation for separating α-olefin oligomers may not necessarily be conducted on all of the substances in the reaction mixture. For instance, when producing 1-hexene from ethylene, small quantities of other α-olefin oligomers such as 1-octene may be left in the reaction mixture without separation. Also, the by-products such as C_{10-20} compounds may be left in the reaction mixture.

In the present invention, the catalyst components such as the chromium compound contained in the reaction mixture may be removed to enhance the purity of the α-olefin oligomers obtained. The various substances obtained from the oligomerization reaction of the α-olefins can be applied to various uses. For instance, 1-hexene, 1-butene and 1-octene, which are recovered from the distilled α-olefin oligomer composition, can be used as a starting monomer for preparation of useful polymers such as linear low-density polyethylene (L-LDPE). Also, 1-butene or butane (C_4) or 1-octene or octane (C_8), for example, can be converted into the corresponding sulfonic acid derivatives by adding hydrogen sulfide and oxidizing the resultant mixture. Salts of such sulfonic acids are useful as surfactants.

Thus, trying to enhance purity of the α-olefin oligomers produced by removing the catalyst components such as the chromium compound contained in the reaction mixture is important for use of the various substances obtained from the oligomerization reactions of α-olefins. Further, depending on the conditions of the distillation separation of the substances, there may arise problems such as deposition of the catalyst components such as the chromium compound on the distillation column, so that it is necessary, from such an aspect, to remove the catalyst components such as the chromium compound contained in the reaction mixture.

Removal of the catalyst components contained in the reaction mixture can be accomplished by contacting the reaction mixture containing the catalyst components with an aqueous acidic or alkaline solution. Removal of the catalyst components is preferably conducted after separation of the by-product in the reaction mixture. Preferred acids are nitric acid, hydrochloric acid and sulfuric acid. Sodium hydroxide is preferably used as the alkali. Such acid or alkali is usually used in the form of a 2 to 20 wt% aqueous solution. Contact of the reaction mixture containing the catalyst components with an acid or alkali solution can be accomplished by using various types of extractor, but it is preferred to use an apparatus composed of a stirring tank and a stationary separating tank. Such tanks may be arranged in a single stage or in multiple stages. The extraction system may be either batchwise or continuos.

The catalyst components which are easily removed by the extraction, although variable depending on the type of extracting agent used (acid or alkali aqueous solution), are mostly metallic substances such as the chromium compound, metal amide and alkylaluminium compound. In the present invention, if necessary, there may be used two stirring tanks to perform extraction with both an acidic aqueous solution and an alkaline aqueous solution.

The extracting conditions are not critical, but when using a stirring tank and a stationary separating tank, the oil layer to aqueous layer ratio in the stirring tank is usually 1 : 0.1 to 10, preferably 1 : 0.5 to 5, the treating temperature is usually 25 to 60°C , preferably 40 to 60°C, and the treating time is usually 5 to 120 minutes, preferably 30 to 90 minutes.

Removal of the catalyst components can be performed at any desired stage after oligomerization. Therefore, the reaction mixture containing the catalyst components is not limited to the reaction mixture which has just been led out of the reaction system, and it may be the reaction mixture from which the main components of α-olefin oligomers and/or solvent have been distilled away. However, when the catalyst components are removed from the reaction mixture from which the great part of the α-olefin oligomers and solvent have been distilled away, there may arise the problems such as deposition of the catalyst components on the distillation column in the distillation separation immediately before the removal operation. Therefore, removal of the catalyst components needs to be conducted at a stage where the catalyst components are not yet concentrated to a high degree after distillation of the reaction mixture.

Metal ions in the acidic or alkaline aqueous solution after extraction treatment can be recovered by a known method, for example, a method using a chelate resin. "Diaion CR10" and "Diaion CR11" (produced by Mitsubishi Chemical Corporation) can be used as a chelate resin. These chelate resins enable efficient recovery of trivalent chromium ions and aluminium ions. To recover metal ions, it is also possible to employ a method in which the desired substances are precipitated as insoluble metals by making use of a pertinent chemical reaction, or a combination of such a method and the method using a chelate resin.

The reaction mixture cleared of the catalyst components is usually washed with water to remove the acid or alkali mixed therein and then separated into α-olefin oligomers and solvent by distillation. Such a distillation separation can be accomplished using a known distillation apparatus. The recovered solvent may be recycled to the reaction system.

In the present invention, α-olefin oligomers other than 1-hexene, for example 1-heptene and 1-octene, can also be produced in a relatively high yield. That is, according to the present invention, it is possible to produce α-olefin oligomers having (n + 4) carbon atoms by carrying out oligomerization of ethylene and an α-olefin having n carbon atoms (wherein n is an integer of not less than 3). In producing α-olefin oligomers having not less than 7 carbon atoms according to said method, the α-olefin and chromium-based catalyst are contacted with each other in a contacting mode where the chromium compound and alkylaluminium compound are inhibited from previously contacting each other. Here, the term "α-olefin" is used to refer to both ethylene and the α-olefin having n carbon atoms. However, when utilizing ethylene and/or an α-olefin having a carbon atoms as a reaction solvent, one of them may be previously introduced into the reactor.

Examples of the α-olefin having n carbon atoms are substituted or un-substituted α-olefins having 3 to 30 carbon atoms, such as propylene, 1-butene, 1-hexene, 1-octene, 3-methyl-1-butene and 4-methyl-1-pentene. In the present invention, the reaction (trimerization reaction) of 2 moles of ethylene and one mole of α-olefin having n carbon atoms is carried out selectively, so that the ratio of said α-olefin to ethylene is not specifically defined. Actually, 0.01 to 1,000 moles of α-olefin having n carbon atoms is used to one mole of ethylene, and an appropriate ratio is selected from this range so that a product having the desired compositional distribution is obtained.

The α-olefin oligomer preparation process of the present invention is especially advantageous, in the following points (i) to (iii), for industrial production of 1-hexene:

(i) The process is capable of producing 1-hexene from ethylene with a high selectivity and in a high yield.

(ii) The oligomerization reaction of ethylene is carried out in a solvent having a higher boiling point than 1-hexene, under a pressure of not less than 10.78×10^5 Pa (10 kg/cm^2(G)), followed by degassing to reduce the pressure to not more than 39.2×10^4 Pa (3 kg/cm^2(G)), and then by-products are separated so that the separation of the by-products is easy to perform. Examples of the reaction solvent having a higher boiling point than 1-hexene are chain or alicylic saturated hydrocarbons such as hexane, heptane, octane, cyclohexane, methylcyclohexane and decalin; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, mesitylene and tetralin; chlorinated chain hydrocarbons such as carbon tetrachloride, dichloroethane, trichloroethane and tetrachloroethane; and chlorinated aromatic hydrocarbons such as chlorobenzene and dichlorobenzene.

Oligomerization of an α-olefin such as ethylene is usually carried out under pressure, and ensuing separation of the by-products is performed with the pressure in the reaction being substantially maintained unchanged. This is because of the following reason. In production of 1-hexene according to a conventional method, the yield of 1-hexene is unsatisfactory and, under certain reaction conditions, a low-boiling point substance (1-butene) is produced as a by-product in a large quantity (about not less than 15 wt%). Accordingly, when the pressure is reduced close to ordinary pressure after the reaction, the cooling load necessary for the distillation separation of 1-butene (boiling point: -6.47°C) from the unreacted ethylene is increased. According to the conventional method, therefore, it is essential to perform separation of the by-products without reducing the pressure after the reaction and then separate 1-butene by distillation, with the pressure being gradually reduced in the ensuing unit operations. However, separation of the by-product polymers under pressure not only necessitates a specific solid/liquid separating device but also has poor operating efficiency. In some cases it may invite additional disadvantages such as blocking of the solid/ liquid separator by the by-product polymers. On the other hand, when 1-hexene is produced according to the α-olefin oligomer production process of the present invention, since 1-hexene can be obtained in a high yield while suppressing the formation of the by-products such as 1-butene, there is no absolute need for recovering 1-butene. When it is this by-product separated by distillation under ordinary pressure, the cooling load necessary for the distillation separation can be lessened remarkably. According to the present invention, the content (the amount produced as a by-product) of 1-butene in the α-olefin oligomer composition can be reduced to not more than 10 wt%, while the content of 1-hexene therein can be increased to not less than 70 wt%, or even to not less than 85 wt%.

According to the present invention, by-product polymers can be separated after reducing the pressure to not more than 39.2 x 10^4 Pa (3 kg/cm^2(G)) by degassing after the reaction. When the pressure is reduced to not more than 39.2 x 10^4 Pa (3 kg/cm^2(G)), use of a relatively simple solid/liquid separator is possible, and there is little possibility of the solid/liquid separator being blocked by the by-product polymers. It is, however, preferable to reduce the pressure to not more than 28.42 x 10^4 Pa (1.9 kg/cm^2(G)), which is specified by law as the limit pressure of a second class high pressure vessel. It is even more preferable to reduce the pressure to not more than 11.76 x 10^4 Pa (0.2 kg/cm^2(G)), under which it is possible to perform substantially the same operations as under ordinary pressure.

(iii) Since the load of the distillation separation of the reaction solvent is small, the benefit of recycling of the solvent is large. When the obtained reaction product composition contains a large number of substances which are hard to separate from each other, the benefit of recycling the reaction solvent is lessened because of the large load of distillation separation of the reaction solvent. In contrast, when 1-hexene is produced according to the α-olefin oligomer production process of the present invention, the content of 1-hexene in the α-olefin oligomer composition obtained is at least 50 wt%, and it can be increased to not less than 75 wt%, or even to not less than 85 wt%. Distillation separation of 1-hexene and the reaction solvent can be accomplished by using a known type of distillation apparatus. The distillation operation may be either batchwise or continuous. In either case, 1-hexene is usually distilled out from the top of the distillation tower. The reaction solvent recovered as the bottom product contains α-olefins other than 1-hexene, but their content is small. In the present invention, therefore, the reaction solvent recovered in the course of distillation separation of 1-hexene can be recycled in the form as it is to the reaction system until the content of α-olefins other than 1-hexene in the reaction system reaches a prescribed concentration. Also, part of the reaction solvent containing such α-olefins may be recycled to the reaction system. It is of course possible to recycle all the reaction solvent recovered in the distillation separation of α-olefins other than 1-hexene. In this case, distillation separation can be accomplished in the same way as described above, but the distillation load is greatly lessened because of the small content of said α-olefins in the reaction solvent.

By the process of the present invention, an α-olefin oligomer composition comprising not less than 85 % by weight of 1-hexene and not more than 15 % by weight of oligomers having not less than 10 carbon atoms and/or polymers may be obtained.

α-Olefin oligomers useful as various types of starting material have been obtained from the oligomerization reaction of α-olefins. The reaction product compositions obtained from the oligomerization reaction of α-olefins, especially the compositions in which the content of 1-hexene is not less than 85 % by weight, are of high industrial utility, and above all, the compositions with a 1-hexene content of not less than 90 % by weight are of particularly high industrial value.

In much of the reaction product compositions (α-olefin oligomer compositions) obtained by conventional methods, the content of the oligomers having 4 to 8 carbon atoms is not more than 75 wt%, that is, such compositions contain the polymers of various numbers of carbon atoms apart from those mentioned above. When, for example, the oligomer having 4 carbon atoms is represented by "C4", a typical example of a composition confirmed in a follow-up test by the present inventors is as follows:

C4:	19%;	C6:	40%;	C8:	16%;	C10:	13%;
C12:	7%;	C14:	3%;	C16:	1%;	C18:	1%

Since this reaction product composition contains many substances which are hard to separate from each other because of their close boiling points and also the content of the oligomers having 4 to 8 carbon atoms is small, the fractionating operation is difficult to carry out and the load of the fractionating process is large.

The α-olefin oligomer compositions provided by the process of the present invention are rich with oligomers having 4 to 8 carbon atoms, so that the load of the fractionating process is small and, therefore, the compositions are usable as various types of starting material to industrial advantage. The compositions are particularly suited for use as starting materials for L-LDPE, which is a very useful resin, and they can even be used in the form as they are as starting materials for the preparation of L-LDPE with certain specific properties. In the preferred α-olefin oligomer compositions, the content of 1-hexene is not less than 85 wt%. In the more preferred α-olefin oligomer compositions, the content of 1-hexene is not less than 90 wt% and the content of each of the origomers and/or polymers having not less than 12 carbon atoms is usually 1 to 2 wt% or less. These α-olefin oligomer compositions can be obtained by removing the starting α-olefins after the oligomerization reaction thereof.

According to the present invention described above, oligomers of α-olefins such as 1-hexene can be produced in a high yield with high selectivity without complicated operations and in an industrially advantageous way. It is also possible to prevent deposition of the by-product polymers on the reactor, distillation column, other incidental equipment and piping. Separation of the by-product polymers is easy and a significant reduction of solvent cost is realized. Further, according to the present invention, purification of α-olefin oligomers to a very high degree can be attained. Still further, according to the present invention, since it is possible to obtain 1-hexene in a high yield, distillation recovery of the reaction solvent to be recycled to the reaction system can be practiced at low load, and separation of the by-product polymers after the reaction can be accomplished under an ordinary pressure or low pressure in an industrially advantageous way. Moreover, according to the present invention, α-olefin oligomer compositions which are reaction product compositions obtained from the oligomerization reaction of α-olefins and which are rich with the oligomers having 4 to 8 carbon atoms can be obtained. Therefore a small load is required for fractionation and hence α-olefin oligomer compositions can be offered as various types of starting material to industrial advantage.

EXAMPLES

The present invention is explained in more detail in the following Examples and Comparative Examples.

Example 1

A 300 ml autoclave dried by a dryer at 150°C was assembled in a hot state and then the atmosphere in the autoclave was replaced with nitrogen in vacuum. A catalyst feed pipe equipped with a rupture plate was previously attached to the autoclave. n-Heptane (45 ml), an n-heptane solution of pyrrole (0.030 mmol) and an n-heptane solution of triethylaluminium (0.800 mmol) were charged to the autoclave, while a n-heptane solution of chromium (III) acetylacetonate (10 mg, 0.029 mmol) was charged to the catalyst feed pipe. The total amount of n-heptane was 50 ml.

First, the autoclave was heated to a temperature of 100°C and then ethylene was introduced thereinto from the catalyst feed pipe at a temperature of 100°C. The rupture plate was ruptured under ethylene pressure and a chromium compound was introduced into the barrel of the autoclave to start the oligomerization of ethylene. Ethylene was introduced until the overall pressure reached 35.28 x 10^5 Pa (35 kg/cm^2(G)), and thereafter the overall pressure was kept at 35.28 x 10^5 Pa (35 kg/cm^2(G)), while maintaining the temperature at 100°C. One hour later, ethanol was injected into the reaction mixture to terminate the reaction.

After releasing ethylene from the autoclave, the by-product polymers (mostly polyethylene) in the reaction mixture were separated by filtration to obtain α-olefin oligomers. The results of compositional analysis of the α-olefin oligomers by gas chromatography are shown along with other data in Table 1.

Examples 2-12

The same procedure as in Example 1 was carried out except that the operating conditions shown in Tables 1-3 were employed. In Example 12, however, 2,5-dimethylpyrrole was used in place of pyrrole. The results are shown in Tables 1-3.

Example 13

The same procedure as in Example 1 was conducted except for a change of the contacting mode between ethylene and chromium-based catalyst, that is, an n-heptane solution of chromium (III) (2-ethylhexanoate) (10 mg, 0.021 mmol) and an n-heptane solution of 2,5-dimethylpyrrole (0.065 mmol) were charged to the autoclave while a n-heptane solution of triethylaluminium (0.400 mmol) was charged to the catalyst feed pipe. The total amount of n-heptane was 50 ml. The results are shown in Table 4.

Examples 14-17

The same procedure as in Example 1 was conducted except that a 2.4-litre autoclave was used to enlarge the scale of the reaction. The results are shown in Tables 4 and 5.

Comparative Example 1

A 300 ml autoclave dried by a 150°C dryer was assembled in a hot state and then the atmosphere in the autoclave was replaced with nitrogen in vacuum. A catalyst feed pipe equipped with a rupture plate was previously attached to this autoclave. n-Heptane (44 ml), an n-heptane solution of chromium (III) 2-ethylhexanoate (10 mg, 0.021 mmol) and an n-heptane solution of triethylaluminium (0.400 mmol) were charged to the autoclave, while a n-heptane solution of 2,5-dimethylpyrrole (0.0650 mmol) was charged to the catalyst feed pipe. The total amount of n-heptane was 50 ml.

First, the autoclave was heated to 100°C and then ethylene was introduced thereinto from the catalyst feed pipe at a temperature of 100°C. The rupture plate was ruptured under ethylene pressure to introduce 2,5-dimethylpyrrole into the barrel of the autoclave to start the oligomerization of ethylene. Ethylene was introduced until the overall pressure reached 35.28 x 10^5 Pa (35 kg/cm^2(G)). Thereafter the overall pressure was kept at 35.28 x 10^5 Pa (35 kg/cm^2(G)), while maintaining the temperature at 100°C. One hour later, ethanol was injected into the reaction mixture to terminate the reaction. After conducting the same operations as in Example 1, α-olefin oligomers were obtained. The results of gas chromatographic analysis of the obtained α-olefin oligomers are shown along with other data in Table 5.

Comparative Example 2

Preparation of Cr compound A:

15 ml of tetrahydrofuran (THF) was added to 0.815 g (20.3 mmol) of NaH, and to the resultant solution was added dropwise 1.4 ml (20 mmol) of pyrrole dissolved in 5 ml of THF. After stirring at room temperature for one hour, the resulting solution was added dropwise to 1.23 g (10 mmol) of $CrCl_2$ suspended in 20 ml of THF. Thereafter 5 ml of THF was added and the resultant mixture was heated under reflux for 20 hours. The precipitate was filtered off, 100 ml of pentane was added to the filtrate and the mixture was left still at a temperature of 5°C. The produced precipitate was collected by filtration and dried to obtain 0.506 g of a dark green powder. The contents of the component elements in this powder were as follows:

Cr:	19.1%;	C:	52.3%;	H:	5.45%;	N:	11.6%.

A 300 ml autoclave dried by a dryer at 150°C was assembled in a hot state and then the atmosphere in the autoclave was replaced with nitrogen in vacuum. To this autoclave were charged n-heptane (44 ml), an n-heptane solution of triethylaluminium (0.120 mmol) and a heptane suspension of Cr compound A (10 mg). The total amount of n-heptane was 50 ml. The resultant mixture was treated at a temperature of 90°C for 30 minutes and then ethylene was introduced at a temperature of 90°C. After this, the overall pressure was kept at 35.28 x 10^5 Pa (35 kg/cm^2(G)) while maintaining the temperature at 100°C. 0.5 hours later, ethanol was injected into the autoclave to terminate the reaction. Thereafter, the same operations as in Example 1 were repeated to recover α-olefin oligomers. The results of gas chromatographic analysis of the α-olefin oligomers are shown along with other data in Table 5.

In the tables shown below, the following abbreviations are used:

HP: n-heptane
CHX: cyclohexane
Cr-1: chromium (III) acetylacetonate
Cr-2: chromium (III) (2,2,6,6-tetramethyl-3,5-heptanedionate)

Cr-3: chromium (III) 2-ethylhexanoate
Cr-4: $CrCl_3 \cdot 3$-pyridine
Cr-5: $(CO)_5Cr(=CCH_3(OCH_3))$
Cr-A: chromium compound synthesized in Comparative Example 2

Also, in the following tables, "contact method A" is a method in which the α-olefin and chromium compound are introduced into a solution containing an amine (pyrrole) and an alkylaluminium compound; "contact method B" is a method in which the α-olefin and alkylaluminium compound are introduced into a solution containing a chromium compound and an amine (pyrrole); and "contact method X" is a method in which the chromium compound and alkylaluminium compound are first heat-treated and then contacted with the α-olefin. The unit of catalyst efficiency is "g- α-olefin/1g-chromium compound", and the unit of catalyst activity is "g- α-olefin/1g-chromium • hr".

Table 1(I)

	Example			
	1	2	3	4
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	HP(50)
Kind of Cr compound	Cr-1	Cr-1	Cr-1	Cr-1
Amount of Cr compound (mg)	10	10	10	10
Molar amount of Cr compound (mmol) (a)	0.029	0.029	0.029	0.029
Molar amount of pyrrole (mmol) (b)	0.030	0.060	0.090	0.050
Molar amount of Et_3Al (mmol) (c)	0.800	0.800	0.800	0.400
Molar ratio of catalyst components (a:b:c)	1:1:28	1:2:28	1:3:28	1:2:14
Reaction temperature (°C)	100	100	100	100
Ethylene pressure Pa (kg/cm^2(G))	35.28×10^5 (35)	35.28×10^5 (35)	35.28×10^5 (35)	35.28×10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	A	A	A	A

Table 1 (II)

	Example			
	1	2	3	4
⟨Product yield (g)⟩	16.0	15.4	14.7	14.2
⟨Compositional distribution (wt%)⟩				
C_4	6.4	6.0	6.2	4.8
C_6 (total)	45.6	45.7	48.4	47.3
1-hexene content in C_6 (wt%)	94.5	94.5	93.6	94.3
C_8	8.2	7.7	7.1	5.3
C_{10-20}	26.0	27.8	22.5	17.8
C_{22-30}	6.3	6.8	6.6	6.5
Wax	2.7	2.8	3.8	12.4
Polyethylene (by-product)	4.8	3.3	5.5	5.9
⟨Catalytic efficiency⟩	1597	1543	1467	1416
⟨Catalytic activity⟩	10740	10380	9860	9520

Table 2(I)

	Example			
	5	6	7	8
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	CHX(50)
Kind of Cr compound	Cr-2	Cr-3	Cr-3	Cr-3
Amount of Cr compound (mg)	10	10	10	10
Cr compound (mmol) (a)	0.017	0.021	0.021	0.021
Pyrrole (mmol) (b)	0.050	0.050	0.065	0.065
Et_3Al (mmol) (c)	0.400	0.400	0.400	0.400
Molar ratio of catalyst components (a:b:c)	1:3:24	1:2:19	1:3:19	1:3:19
Reaction temperature (°C)	100	100	100	100
Ethylene pressure Pa (kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 35
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	A	A	A	A

Table 2 (II)

	Example			
	5	6	7	8
〈Product yield (g)〉	9.8	6.5	7.3	11.9
〈Compositional disposition (wt%)				
C_4	10.6	9.5	10.5	16.3
C_6 (total)	58.8	68.7	61.0	50.0
1-hexene content in C_6 (wt%)	92.0	92.4	92.6	92.1
C_8	8.8	6.9	8.0	11.2
C_{10-20}	20.5	13.2	19.7	21.8
C_{22-30}	1.0	0.7	0.8	0.5
Wax	0.1	0.0	0.1	0.0
Polyethylene (by-product)	0.3	1.0	0.8	0.2
〈Catalytic efficiency〉	979	646	734	1187
〈Catalytic activity〉	11350	6000	6790	10990

Table 3 (I)

	Example			
	9	10	11	12
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	HP(50)
Kind of Cr compound	Cr-3	Cr-4	Cr-5	Cr-3
Amount of Cr compound (mg)	10	10	5	10
Cr compound (mmol) (a)	0.021	0.025	0.020	0.021
Pyrrole (mmol) (b)	0.065	0.075	0.060	0.065
Et_3Al (mmol) (c)	4.160	0.510	0.400	0.400
Molar ratio of catalyst components (a:b:c)	1:3:198	1:3:20	1:3:20	1:3:19
Reaction temperature (°C)	100	100	60	100
Ethylene pressure Pa (kg/cm^2(G))	35.28×10^5 (35)	35.28×10^5 (35)	35.28×10^5 (35)	35.28×10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	A	A	A	A

Table 3 (II)

	Example			
	9	10	11	12
〈Product yield (g)〉	13.3	7.4	1.9	27.0
〈Compositional distribution (wt%)〉				
C_4	13.2	4.9	8.0	10.0
C_6 (total)	66.6	71.5	81.2	60.4
1-hexene content in C_6 (wt%)	93.1	92.9	94.5	90.1
C_8	7.8	5.0	3.8	6.0
C_{10-20}	11.8	16.4	7.0	23.6
C_{22-30}	0.1	0.8	0.0	0.0
Wax	0.0	0.1	0.0	0.0
Polyethylene (by-product)	0.5	1.4	0.0	0.0
〈Catalytic efficiency〉	1332	744	388	2695
〈Catalytic activity〉	12330	5680	1868	25000

Table 4 (I)

	Example			
	13	14	15	16
Kind of solvent (amount:ml)	HP(50)	HP(1000)	HP(1000)	HP(1000)
Kind of Cr compound	Cr-3	Cr-3	Cr-3	Cr-3
Amount of Cr compound (mg)	10	200	200	200
Cr compound (mmol) (a)	0.021	0.420	0.420	0.420
Pyrrole (mmol) (b)	0.065	1.244	1.244	1.244
Et_3Al (mmol) (c)	0.400	2.000	2.000	2.000
Molar ratio of catalyst components (a:b:c)	1:3:19	1:3:5	1:3:5	1:3:5
Reaction temperature (°C)	100	60	40	30
Ethylene pressure Pa (kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	B	A	A	A

Table 4 (II)

	Example			
	13	14	15	16
⟨Product yield (g)⟩	32.5	57.4	41.8	45.2
⟨Compositional distribution (wt%)⟩				
C_4	2.0	2.7	3.0	4.1
C_6 (total)	71.9	90.2	92.1	89.3
1-hexene content in C_6 (wt%)	92.7	99.2	99.5	99.4
C_8	1.7	2.5	2.7	3.5
C_{10-20}	18.6	4.3	1.4	1.9
C_{22-30}	5.8	0.1	0.0	0.0
Wax	0.0	0.0	0.0	0.0
Polyethylene (by-product)	0.0	0.4	0.7	1.1
⟨Catalytic efficiency⟩	3252	287	209	226
⟨Catalytic activity⟩	30100	2758	2012	2174

Table 5 (I)

	Example	Comparative Example	
	17	1	2
Kind of solvent (amount:ml)	HP (1000)	HP (50)	HP (50)
Kind of Cr compound	Cr-3	Cr-3	Cr-A
Amount of Cr compound (mg)	200	10	10
Cr compound (mmol) (a)	0.420	0.021	-
Pyrrole (mmol) (b)	1.659	0.065	-
Et_3Al (mmol) (c)	2.000	0.400	0.120
Molar ratio of catalyst components (a:b:c)	1:4:5	1:3:19	-
Reaction temperature (°C)	60	100	100
Ethylene pressure Pa (kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0
Contacting method	A	X	X

Table 5 (II)

	Example	Comparative Example	
	17	1	2
⟨Product yield (g)⟩	41.5	0.8	0.6
⟨Compositional distribution (wt%)⟩			
C_4	1.4	3.5	8.3
C_6 (total)	92.3	85.3	78.7
1-hexene content in C_6 (wt%)	99.6	90.6	85.0
C_8	2.1	1.6	tr.
C_{10-20}	3.5	8.1	tr.
C_{22-30}	0.2	0.4	0.0
Wax	0.0	0.0	0.0
Polyethylene (by-product)	0.4	1.1	5.1
⟨Catalytic efficiency⟩	208	80	60
⟨Catalytic activity⟩	1997	739	628

Example 18

A pipe reactor having a pressure coiled pipe of 6 mm inner diameter an 10.5 m length, which is disposed inside the jacket was used. A catalyst feed pipe was connected to a point 0.5 m from the front end of said coiled pipe. The atmosphere of the pipe reactor was replaced with nitrogen in vacuum and then the interior temperature of the jacket was kept at 100°C.

n-Heptane, an n-heptane solution of pyrrole (0.017 mmol/ml) and an n-heptane solution of triethylaluminium (0.453 mmol/ml) were introduced continuously from the front end of said pipe reactor at the rates of 253 ml/hr, 10 ml/hr and 10 ml/hr, respectively, while a n-heptane solution of chromium (III) acetylacetonate (5.6 mg, 0.0164 mmol/ml) was introduced continuously together with ethylene (100°C) from the catalyst feed pipe at a rate of 10 ml/hr. The reaction pressure was adjusted to 35.28 x 10^5 Pa (35 kg/cm^2(G)) by ethylene pressure. The introduction time of the respective components was controlled so that retention time was one hour. The reaction mixture effusing from the pipe reactor was introduced into a pressure vessel separately provided in connection to the pipe reactor. Ethanol was injected into the reaction mixture in the pressure vessel to terminate the reaction.

After releasing the pressure from the vessel, the by-product polymers (mostly polyethylene) in the reaction mixture were separated by filtration to obtain α-olefin oligomers. The results of compositional analysis of the obtained α-olefin oligomers by gas chromatography are shown along with other data in Table 6.

Examples 19-29

The same procedure as in Example 18 was carried out except that the reaction conditions shown in Tables 6-8 were employed. In Example 29, however, 2,5-dimethylpyrrole was used in place of pyrrole. The results are shown in Tables 5-8.

Example 30

The same procedure as in Example 18 was conducted except for a change of the contacting mode between the ethylene and chromium-based catalyst, that is, n-heptane, an n-heptane solution of chromium (III) (2-ethylhexanoate) (107.6 mg, 0.226 mmol/ml) and an n-heptane solution of 2,5-dimethylpyrrole (0.012 mmol/ml) were introduced continuously from the front end of the pipe reactor at the rates of 253 ml/hr, 10 ml/hr and 10 ml/hr, respectively, while a heptane solution of triethylaluminium (0.037 mmol/ml) was introduced continuously together with ethylene (100°C) from the catalyst feed pipe at a rate of 10 ml/hr. The results are shown in Table 9.

Examples 31-34

There was used as reactor a multi-stage mixing tank having 2 sets of 2.4 litre (1 litre fluid capacity) autoclaves arranged in series to each other and connected by an overflow pipe. Each of the autoclaves, after being dried by a dryer at 150°C, was assembled in a hot state and then the atmosphere in each autoclave was replaced with nitrogen in vacuum. n-Heptane, an n-heptane solution of pyrrole (0.124 mmol/ml) and an n-heptane solution of triethylaluminium (0.200 mmol/ml) were introduced continuously into the first autoclave at the rates of 970 ml/hr, 10 ml/hr and 10 ml/hr, respectively, and the obtained mixed solution was overflowed to the second autoclave. At the same time, an n-heptane solution of chromium (III) acetylacetonate (14 mg, 0.042 mmol/ml) was introduced continuously together with ethylene into the second autoclave at a rate of 10 ml/hr. The reaction conditions shown in Tables 4 and 5 were employed. The reaction pressure was adjusted with ethylene pressure, and the retention time was controlled by the introduction rates of the feedstocks. The reaction mixture effusing from the overflow pipe of the second autoclave was introduced into a pressure vessel provided separately in connection to the overflow pipe. Ethanol was injected into the reaction mixture in the pressure vessel to terminate the reaction.

After releasing the pressure from the vessel, the by-product polymers (mostly polyethylene) in the reaction mixture were separated by filtration to obtain α-olefin oligomers. The results of compositional analysis of the α-olefin oligomers are shown along with other data in Tables 9 and 10.

Table 6(I)

	Example			
	18	19	20	21
Kind of solvent	HP	HP	HP	HP
Kind of Cr compound	Cr-1	Cr-1	Cr-1	Cr-1
Amount of Cr compound (mg/hour)	56	56	56	56
Molar amount of Cr compound (mmol/hour) (a)	0.164	0.164	0.164	0.164
Molar amount of pyrrole (mmol/hour) (b)	0.170	0.340	0.510	0.283
Molar amount of Et_3Al (mmol/hour) (c)	4.530	4.530	4.530	2.260
Molar ratio of catalyst components (a:b:c)	1:1:28	1:2:28	1:3:28	1:2:14
Reaction temperature (°C)	100	100	100	100
Ethylene pressure Pa (kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	A	A	A	A

Table 6(II)

	Example			
	18	19	20	21
⟨Product yield (g/hour)⟩	90.6	87.2	83.2	80.4
⟨Compositional distribution (wt%)⟩				
C_4	6.0	6.3	6.0	4.5
C_6 (total)	45.8	45.2	48.6	47.6
1-hexene content in C_6 (wt%)	94.7	94.2	93.3	94.3
C_8	8.0	7.8	7.3	5.5
C_{10-20}	26.2	27.9	22.3	17.7
C_{22-30}	6.5	6.7	6.7	6.4
Wax	2.6	2.9	3.4	12.7
Polyethylene (by-product)	4.9	3.2	5.7	5.6
⟨Catalytic efficiency⟩	1595	1546	1465	1419
⟨Catalytic activity⟩	10743	10382	9863	9526

Table 7(I)

	Example			
	21	23	24	25
Kind of solvent	HP	HP	HP	CHX
Kind of Cr compound	Cr-2	Cr-3	Cr-3	Cr-3
Amount of Cr compound (mg/hour)	5.6	5.7	5.7	5.7
Molar amount of Cr compound (mmol/hour) (a)	0.096	0.119	0.119	0.119
Molar amount of pyrrole (mmol/hour) (b)	0.283	0.283	0.368	0.368
Molar amount of Et_3Al	2.260	2.260	2.260	2.260
(mmol/Hr) (c) Molar ratio of catalyst components (a:b:c)	1:3:24	1:2:19	1:3:19	1:3:19
Reaction temperature (°C)	100	100	100	100
Ethylene pressure Pa (kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	A	A	A	A

Table 7(II)

	Example			
	21	23	24	25
⟨Product yield (g/hour)⟩	55.5	36.8	41.3	67.4
⟨Compositional distribution (wt%)⟩				
C_4	10.8	9.0	10.1	16.5
C_6 (total)	58.6	68.7	61.4	50.0
1-hexene content in C_6 (wt%)	92.2	92.6	92.5	92.4
C_8	8.8	7.0	8.2	11.4
C_{10-20}	20.4	13.4	19.5	21.8
C_{22-30}	1.0	0.9	0.8	0.4
Wax	0.1	0.0	0.1	0.1
Polyethylene (by-product)	0.3	1.0	0.8	0.2
⟨Catalytic efficiency⟩	976	648	736	1189
⟨Catalytic activity⟩	11355	6005	6793	10995

Table 8(I)

	Example			
	26	27	28	29
Kind of solvent	HP	HP	HP	HP
Kind of Cr compound	Cr-3	Cr-4	Cr-5	Cr-3
Amount of Cr compound (mg/hour)	5.7	5.7	5.7	5.7
Molar amount of Cr compound (mmol/hour) (a)	0.119	0.142	0.113	0.119
Molar amount of pyrrole (mmol/hour) (b)	0.368	0.425	0.340	0.368
Molar amount of Et_3Al (mmol/hour) (c)	23.50	2.890	2.260	2.260
Molar ratio of catalyst components (a:b:c)	1:3:198	1:3:20	1:3:20	1:3:19
Reaction temperature (°C)	100	100	60	100
Ethylene pressure Pa (kg/cm^2(G))	35.28×10^5 (35)	35.28×10^5 (35)	35.28×10^5 (35)	35.28×10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	A	A	A	A

Table 8(II)

	Example			
	26	27	28	29
⟨Product yield (g/hour)⟩	75.3	41.9	10.7	152.8
⟨Compositional distribution (wt%)⟩				
C_4	13.0	4.6	8.3	10.3
C_6 (total)	66.9	71.8	81.0	60.1
1-hexene content in C_6 (wt%)	93.1	92.9	94.5	90.1
C_8	7.7	4.9	3.7	5.8
C_{10-20}	11.7	16.5	7.0	23.7
C_{22-30}	0.1	0.6	0.0	0.1
Wax	0.1	0.1	0.0	0.0
Polyethylene (by-product)	0.5	1.6	0.1	0.0
⟨Catalytic efficiency⟩	1335	742	387	2690
⟨Catalytic activity⟩	12335	5683	1869	25019

Table 9(I)

	Example			
	30	31	32	33
Kind of solvent	HP	HP	HP	HP
Kind of Cr compound	Cr-3	Cr-3	Cr-3	Cr-3
Amount of Cr compound (mg/hour)	5.7	200	200	200
Molar amount of Cr compound (mmol/hour) (a)	0.119	0.420	0.420	0.420
Molar amount of pyrrole (mmol/hour) (b)	0.368	1.244	1.244	1.244
Molar amount of Et_3Al (mmol/hour) (c)	2.260	2.000	2.000	2.000
Molar ratio of catalyst components (a:b:c)	1:3:19	1:3:5	1:3:5	1:3:5
Reaction temperature (°C)	100	60	40	30
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contacting method	B	A	A	A

Table 9(II)

	Example			
	30	31	32	33
⟨Product yield (g/hour)⟩	184.0	57.4	41.8	45.2
⟨Compositional distribution (wt%)⟩				
C_4	2.3	2.4	3.3	4.5
C_6 (total)	71.6	90.5	92.1	89.0
1-hexene content in C_6 (wt%)	92.7	99.2	99.5	99.4
C_8	1.5	2.2	2.9	3.6
$C_{10\text{-}20}$	18.8	4.6	1.3	1.8
$C_{22\text{-}30}$	5.7	0.1	0.1	0.1
Wax	0.1	0.1	0.0	0.0
Polyethylene (by-product)	0.0	0.3	0.5	1.1
⟨Catalytic efficiency⟩	3250	285	211	220
⟨Catalytic activity⟩	30111	2761	2015	2176

Table 10(I)

	Example
	34
Kind of solvent	HP
Kind of Cr compound	Cr-3
Amount of Cr compound (mg/hour)	200
Molar amount of Cr compound (mmol/hour) (a)	0.420
Molar amount of pyrrole (mmol/hour) (b)	1.659
Molar amount of Et_3Al (mmol/hour) (c)	2.000
Molar ratio of catalyst components (a:b:c)	1:4:5
Reaction temperature (°C)	60
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)
Reaction time (Hr)	1.0
Contacting method	A

Table 10(II)

	Example
	34
⟨Product yield (g/hour)⟩	41.5
⟨Compositional distribution (wt%)⟩	
C_4	1.1
C_6 (total)	92.6
1-hexene content in C_6 (wt%)	99.6
C_8	2.5
C_{10-20}	3.1
C_{22-30}	0.1
Wax	0.0
Polyethylene (by-product)	0.5
⟨Catalytic efficiency⟩	213
⟨Catalytic activity⟩	2011

Example 35

n-Heptane (47 ml), an n-heptane solution of pyrrole (0.063 mmol), an n-heptane solution of triethylaluminium (0.400 mmol) and 1,5-cyclooctadiene (9.410 mmol) as additional component were charged to the same autoclave as used in Example 1, while a heptane solution of chromium (III) (2-ethylhexanoate) (10 mg, 0.021 mmol) was charged to the catalyst feed pipe. The total amount of n-heptane was 50 ml. Thereafter the same operations as in Example 1 were performed, and the oligomerization reaction of ethylene was conducted under the conditions shown in Table 11. The results of gas chromatographic analysis of the obtained α-olefin oligomers are shown along with other data in Table 11.

The symbol "a-1" indicates that the additional component in Table 11 is 1,5-cyclooctadiene.

Table 11(I)

	Example
	35
Kind of solvent (amount:ml)	HP(50)
Kind of Cr compound	Cr-3
Amount of Cr compound (mg/hour)	10
Molar amount of Cr compound (mmol/hour) (a)	0.021
Molar amount of pyrrole (mmol/hour) (b)	0.063
Molar amount of Et_3Al (mmol/hour) (c)	0.400
Molar ratio of catalyst components (a:b:c)	1:3:19
Kind of additional component	a-1
Molar amount of additional substance (mmol)	9.410
Reaction temperature (°C)	100

Table 11(II)

	Example
	35
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)
Reaction time (Hr)	1.0
Contact method	A
⟨Product yield (g/hour)⟩	9.2
⟨Compositional distribution (wt%)⟩	
C_4	15.1
C_6 (total)	52.3
1-hexene content in C_6 (wt%)	95.0
C_8	12.3
C_{10-20}	20.1
C_{22-30}	0.1
Wax	0.0
Polyethylene (by-product)	0.1
⟨Catalytic efficiency⟩	922
⟨Catalytic activity⟩	8583

Examples 36-39

The same procedure as in Example 35 was conducted except for a change of the additional component and employment of the reaction conditions shown in Table 12. In Example 39, mesitylene was used as an additional component in place of n-heptane (47 ml). The results of gas chromatographic analysis of the obtained α-olefin oligomers are shown along with other data in Table 12.

The symbols indicating the additional components in Table 12 denote the following:

b-1: mesitylene
c-1: 1,3,5-tri-tert-butylbenzene
d-1: hexamethylbenzene

Table 12(I)

	Example			
	36	37	38	39
Kind of solvent (amount:ml)	HP(49)	HP(49)	HP(49)	HP(3)
Kind of Cr compound	Cr-3	Cr-3	Cr-3	Cr-3
Amount of Cr compound (mg/Hr)	10	10	10	10
Molar amount of Cr compound (mmol/hour) (a)	0.021	0.021	0.021	0.021
Molar amount of pyrrole (mmol/hour) (b)	0.063	0.063	0.063	0.063
Molar amount of Et_3Al (mmol/hour) (c)	0.400	0.400	0.400	0.400
Molar ratio of catalyst components (a:b:c)	1:3:19	1:3:19	1:3:19	1:3:19
Kind of additional component	b-1	c-1	d-1	b-1
Molar amount of additional substance (mmol)	9.410	9.410	9.410	340.0
Reaction temperature (°C)	100	100	100	100

Table 12(II)

	Example			
	36	37	38	39
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contact method	A	A	A	A
⟨Product yield (g/hour)⟩	9.1	10.8	8.9	6.9
⟨Compositional distribution (wt%)⟩				
C_4	15.8	14.4	13.8	26.7
C_6 (total)	48.1	52.8	55.5	28.8
1-hexene content in C_6 (wt%)	96.1	94.1	95.5	98.1
C_8	13.3	10.9	10.6	16.8
C_{10-20}	22.0	21.1	19.1	26.4
C_{22-30}	0.5	0.3	0.6	0.7
Wax	0.0	0.0	0.0	0.0
Polyethylene (by-product)	0.2	0.4	0.4	0.5
⟨Catalytic efficiency⟩	910	1076	892	689
⟨Catalytic activity⟩	8425	9964	8258	6382

Examples 40-47

The same procedure as in Example 35 was conducted except for a change of the additional component and employment of the reaction conditions shown in Tables 13 and 14. In Example 42, toluene was not charged to the autoclave as an additional component, and 1 ml (9.41 mmol) of toluene was used for making a solution of chromium (III) (2-

ethylhexanoate) and was charged to a feed pipe. In Examples 46 and 47, 2,5-dimethylpyrrole was used in place of pyrrole. The results of gas chromatographic analysis of the obtained α-olefin oligomers are shown along with other data in Tables 13 and 14.

The symbols indicating the additional components in Tables 13 and 14 denote the following.

e-1: benzene
f-1: toluene
g-1: m-xylene

Table 13(I)

	Example			
	40	41	42	43
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	HP(50)
Kind of Cr compound	Cr-3	Cr-3	Cr-3	Cr-3
Amount of Cr compound (mg/hour)	10	10	10	10
Molar amount of Cr compound (mmol/hour) (a)	0.021	0.021	0.021	0.021
Molar amount of pyrrole (mmol/hour) (b)	0.063	0.063	0.063	0.063
Molar amount of Et_3Al (mmol/hour) (c)	0.400	0.400	0.400	0.800
Molar ratio of catalyst components (a:b:c)	1:3:19	1:3:19	1:3:19	1:3:38
Kind of additional component	e-1	f-1	f-1	f-1
Molar amount of additional substance (mmol)	9.410	9.410	9.410	9.410
Reaction temperature (°C)	100	100	100	100

Table 13(II)

	Example			
	40	41	42	43
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contact method	A	A	A	A
⟨Product yield (g/hour)⟩	6.9	6.3	6.4	9.0
C_4	18.8	8.3	22.5	15.0
C_6 (total)	47.8	63.0	49.8	58.2
1-hexene content in C_6 (wt%)	96.1	96.5	96.7	96.0
C_8	13.4	7.9	13.4	10.3
C_{10-20}	19.3	19.1	13.8	15.4
C_{22-30}	0.6	1.5	0.3	0.6
Wax	0.0	0.0	0.0	0.0
Polyethylene (by-product)	0.1	0.4	0.2	0.5
⟨Catalytic efficiency⟩	694	625	644	902
⟨Catalytic activity⟩	6430	5783	5960	8359

Table 14(I)

	Example			
	44	45	46	47
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	HP(50)
Kind of Cr compound	Cr-1	Cr-3	Cr-3	Cr-3
Amount of Cr compound (mg/hour)	10	10	5	10
Molar amount of Cr compound (mmol/hour) (a)	0.021	0.028	0.010	0.021
Molar amount of pyrrole (mmol/hour) (b)	0.085	0.063	0.031	0.063
Molar amount of Et_3Al (mmol/hour) (c)	0.570	0.400	0.200	0.200
Molar ratio of catalyst components (a:b:c)	1:3:19	1:2:14	3:3:20	1:3:19
Kind of additional component	f-1	g-1	f-1	f-1
Molar amount of additional substance (mmol)	9.410	9.410	9.410	47.05
Reaction temperature (°C)	100	100	90	90

Table 14(II)

	Example			
	44	45	46	47
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0	1.0
Contact method	A	A	A	A
⟨Product yield (g/hour)⟩	9.6	6.0	4.6	5.2
⟨Compositional distribution (wt%)⟩				
C_4	5.1	18.9	56.8	57.9
C_6 (total)	49.4	48.7	32.1	29.8
1-hexene content in C_6 (wt%)	94.9	96.3	96.5	98.3
C_8	6.0	12.7	7.3	8.5
C_{10-20}	22.6	18.6	3.5	3.6
C_{22-30}	9.3	0.4	0.0	0.1
Wax	0.0	0.0	0.0	0.0
Polyethylene (by-product)	7.7	0.5	0.1	0.2
⟨Catalytic efficiency⟩	964	596	909	523
⟨Catalytic activity⟩	6470	5514	8420	4843

Examples 48-58 and Reference Example 1

The same procedure as in Example 35 was conducted except that the additional component and employment of the reaction conditions were changed as shown in Tables 15-17. The results of gas chromatographic analysis of the

obtained α-olefin oligomers are shown along with other data in Tables 15-17.

In Tables 15-17, "h-1" indicates the additional] component is tris(pentafluorophenyl)borane. "Contact method A_1" is a method in which the α-olefin, chromium compound and additional component {tris(pentafluorophenyl)borane: $B(C_6F_5)_3$} are introduced into a solution containing pyrrole and alkylaluminium compound; "contact method A_2" is a method in which the α-olefin and chromium compound are introduced into a solution containing pyrrole, alkylaluminium compound and additional substance; "contact method D_1" is a method in which the α-olefin, chromium compound and pyrrole are introduced into a solution containing alkylaluminium compound and additional substance; and "contact method F" is a method in which the α-olefin is introduced into a solution prepared by successively feeding the additional component, alkylaluminium compound, pyrrole and chromium compound.

Table 15(I)

	Example			Reference Example 1
	48	49	50	
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	HP(50)
Kind of Cr compound	Cr-1	Cr-1	Cr-1	Cr-1
Amount of Cr compound (mg/hour)	10	10	10	10
Molar amount of Cr compound (mmol/hour) (a)	0.021	0.021	0.021	0.021
Molar amount of pyrrole (mmol/hour) (b)	0.060	0.060	0.060	0.060
Molar amount of Et_3Al (mmol/hour) (c)	0.400	0.400	0.400	0.400
Molar ratio of catalyst components (a:b:c)	1:3:19	1:3:19	1:3:19	1:3:19
Kind of additional component	h-1	h-1	h-1	h-1
Molar amount of additional substance (mmol)	0.020	0.020	0.100	0.020
Reaction temperature (°C)	100	100	100	100

Table 15(II)

	Example			Comparative Example 3
	48	49	50	
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	0.25	0.25	0.25	0.25
Contacting method	A_1	A_2	A_2	F
⟨Product yield (g/hour)⟩	14.4	14.4	38.0	13.7
⟨Compositional distribution (wt%)⟩				
C_4	1.7	1.9	0.2	1.4
C_6 (total)	79.5	74.5	83.2	80.3
1-hexene content in C_6 (wt%)	94.6	94.6	94.4	94.9
C_8	2.7	3.0	0.5	2.1
C_{10-20}	13.9	17.9	15.2	14.0
C_{22-30}	1.4	2.0	0.5	1.3
Wax	0.0	0.0	0.0	0.0
Polyethylene (by-product)	0.5	0.3	0.3	0.7
⟨Catalytic efficiency⟩	1439	1439	3799	1367
⟨Catalytic activity⟩	53313	53328	140699	50616

Table 16(I)

	Example			
	51	52	53	54
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	HP(50)
Kind of Cr compound	Cr-1	Cr-1	Cr-1	Cr-1
Amount of Cr compound (mg/hour)	10	10	10	10
Molar amount of Cr compound (mmol/hour) (a)	0.021	0.021	0.021	0.021
Molar amount of pyrrole (mmol/hour) (b)	0.060	0.060	0.060	0.060
Molar amount of Et_3Al (mmol/hour) (c)	0.400	0.400	0.400	0.400
Molar ratio of catalyst components (a:b:c)	1:3:19	1:3:19	1:3:19	1:3:19
Kind of additional component	h-1	h-1	h-1	h-1
Molar amount of additional substance (mmol)	0.020	0.100	0.100	0.060
Reaction temperature (°C)	100	60	45	100

Table 16(II)

	Example			
	51	52	53	54
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	0.25	0.25	0.25	0.25
Contacting method	D_1	D_1	D_1	D_1
⟨Product yield (g/hour)⟩	19.1	23.0	24.7	33.2
⟨Compositional distribution (wt%)⟩				
C_4	1.2	0.3	0.7	0.3
C_6 (total)	79.1	85.5	81.8	82.8
1-hexene content in C_6 (wt%)	94.4	95.3	94.8	94.2
C_8	1.9	0.7	0.9	0.6
C_{10-20}	15.7	11.3	14.3	15.2
C_{22-30}	1.1	0.3	0.4	0.5
Wax	0.0	0.1	0.2	0.1
Polyethylene (by-product)	0.7	1.8	1.8	0.5
⟨Catalytic efficiency⟩	1910	2302	2476	3318
⟨Catalytic activity⟩	70729	85272	91720	122885

Table 17(I)

	Example			
	55	56	57	58
Kind of solvent (amount:ml)	HP(50)	HP(50)	HP(50)	HP(50)
Kind of Cr compound	Cr-1	Cr-1	Cr-1	Cr-1
Amount of Cr compound (mg/hour)	10	10	10	10
Molar amount of Cr compound (mmol/hour) (a)	0.021	0.021	0.021	0.021
Molar amount of pyrrole (mmol/hour) (b)	0.060	0.060	0.060	0.060
Molar amount of Et_3Al (mmol/hour) (c)	0.400	0.400	0.200	0.400
Molar ratio of catalyst components (a:b:c)	1:3:19	1:3:19	1:3:10	1:3:19
Kind of additional component	h-1	h-1	h-1	h-1
Molar amount of additional substance (mmol)	0.004	0.004	0.004	0.004
Reaction temperature (°C)	100	100	100	100

Table 17(II)

	Example			
	55	56	57	58
Ethylene pressure Pa(kg/cm^2(G))	35.28 x 10^5 35	69.62 x 10^5 70	35.28 x 10^5 35	35.28 x 10^5 35 (H_2: 44.1 x 10^4 Pa (3.5 kg/cm^2 (G))
Reaction time (Hr)	0.25	0.25	0.25	0.25
Contact method	D_1	D_1	D_1	D_1
⟨Product yield (g/hour)⟩	6.7	15.9	3.9	14.9
⟨Compositional distribution (wt%)⟩				
C_4	2.4	3.5	3.6	1.9
C_6 (total)	78.7	78.2	79.4	78.8
1-hexene content in C_6 (wt%)	94.5	95.0	94.3	92.0
C_8	3.5	3.9	3.6	2.2
C_{10-20}	14.2	13.9	12.2	16.7
C_{22-30}	1.1	0.5	0.8	0.4
Wax	0.1	0.0	0.1	0.0
Polyethylene (by-product)	0.1	0.1	0.3	0.1
⟨Catalytic efficiency⟩	667	1588	386	1488
⟨Catalytic activity⟩	24711	58797	14303	55111

Example 59

n-Heptane (980 ml), an n-heptane solution of pyrrole (1.244 mmol) and an n-heptane solution of triethylaluminium (8.000 mmol) were charged to a 2.4 litre autoclave which was the same as used in Example 1 while chromium (III) 2-ethylhexanoate (200 mg, 0.420 mmol) dissolved in n-heptane was charged to the catalyst feed pipe. An n-heptane solution of an antistatic agent A specified below (1 mg/l) also charged to the autoclave.

Antistatic agent A: "ASA-3" (produced by Shell Chemical Co., Ltd.)

The composition thereof comprises 20 wt% of chromium (III) alkylsalicylate having a C_{14-18} alkyl group, 10 wt% of the calcium salt of di-2-ethylhexyl sulfosuccinate, 45 wt% of a copolymer (high polymeric electrolyte) of 2-methyl-5-vinylpyridine and methacrylic acid C_{17} alkyl ester.

First, the autoclave was heated to a temperature of 40°C and then ethylene was introduced thereinto from the catalyst feed pipe at a temperature of 40°C. The rupture plate was ruptured under ethylene pressure, introducing the chromium compound into the barrel of the autoclave to start oligomerization of ethylene. Ethylene was introduced until the overall pressure reached 35.28 x 10^5 Pa (35 kg/cm^2(G)). Thereafter the overall pressure was kept at 35.28 x 10^5 Pa (35 kg/cm^2(G)), while maintaining the temperature at 40°C. One hour later, ethanol was injected into the reaction mixture to terminate the reaction.

Then the same operations as in Example 1 were repeated to obtain α-olefin oligomers. In this Example, no deposition of the by-product polymers took place on the inner wall of the autoclave. The results of compositional analysis of the obtained α-olefin oligomers by gas chromatography are shown along with other data in Table 18.

Examples 60 and 61

The same procedure as in Example 59 was conducted except for a change of reaction temperature, solvent and antistatic agent as shown in Table 18. The results of gas chromatographic analysis of the obtained α-olefin oligomers

are shown along with other data in Table 18. In both Examples, no deposition of the by-product polymers was observed on the inner wall of the autoclave. In the table, antistatic agents "B" and "C" are as specified below:

Antistatic agent B: "Stadis 450" (produced by E.I. Du Pont de Neymours & Co.)

The composition thereof comprises 14 wt% of polybutene sulfate, 3 wt% of aminoethanolepichlorohydrin polymer, 13 wt% of alkylbenzenesulfonic acid, 70 wt% of toluene and trace amounts of a quaternary ammonium salt of an aliphatic alkyl and isopropyl alcohol.

Antistatic agent C: "Stadis 425" (produced by E.I. Du Pont de Neymours & Co.)

The composition thereof comprises 2-7 wt% of polyaminopolyol, 2-8 wt% of dodecylbenzenesulfonic acid, 60-70 wt% of kerosine, 10-20 wt% of toluene, less than 0.017 wt% of benzene and 2-7 wt% of a mixed aromatic solvent (C_{9-17}).

Table 18(I)

	Example		
	59	60	61
Antistatic agent	A	B	C
Kind of solvent (amount:liter)	HP(1)	HP(1)	HP(1)
Reaction temperature (°C)	40	60	60
Ethylene pressure Pa(Kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0	1.0
⟨Product yield (g/hour)⟩	88.2	102.7	123.8
⟨Compositional distribution (wt%)⟩			
C_4	12.2	15.3	18.0
C_6 (total)	74.7	74.2	71.6
1-hexene content in C_6 (wt%)	96.2	95.7	96.0
C_8	2.1	3.1	3.2
C_{10-20}	20.2	6.8	6.7
C_{22-30}	0.1	0	0

Table 18(II)

	Example		
	59	60	61
Wax	0	0	0
Polyethylene (by-product)	0.7	0.6	0.4
⟨Deposition efficiency⟩	None	None	None
⟨Catalytic efficiency⟩	441	513	619
⟨Catalytic activity⟩	4239	4936	5952

Example 62

A 2.4-litre autoclave dried by a dryer at 150°C was assembled in a hot state and then the atmosphere in the autoclave was replaced with nitrogen in vacuum. A catalyst feed pipe equipped with a rupture plate and a stirrer equipped with a one-stage simple paddle-type (flat vane-type) blade had been attached to the autoclave. n-Heptane (980 ml), an n-heptane solution of pyrrole (1.244 mmol) and an n-heptane solution of triethylaluminum (8.000 mmol) were charged to the autoclave while an n-heptane solution of chromium (III) 2-ethylhexanoate (200 mg, 0.420 mmol) was charged to the catalyst feed pipe. The total amount of n-heptane was 1 litre.

First, the autoclave was heated to a temperature of 40°C and then ethylene was introduced thereinto from the catalyst feed pipe at a temperature of 40°C. The rupture plate was ruptured under ethylene pressure to introduce the chromium compound into the autoclave, thus starting the oligomerization of ethylene. The stirrer was operated at 400 r.p.m. and ethylene was introduced until the overall pressure reached 35.28×10^5 Pa (35 kg/cm^2(G)). Thereafter the overall pressure was kept at 35.28×10^5 Pa (35 kg/cm^2(G)), while maintaining the temperature at 40°C. One hour later, ethanol was injected into the autoclave to terminate the reaction.

After releasing ethylene from the autoclave, the by-product polymers (mostly polyethylene) in the reaction mixture were separated by filtration to obtain α-olefin oligomers. In this example, the by-product polymers were granular (100-300 μm grain size) and the filtering operation could be performed very smoothly. The results of gas chromatographic analysis of the obtained α-olefin oligomers are shown along with other data in Table 19.

Examples 63 and 64

The same procedure as in Example 62 was conducted except for a change of reaction temperature and stirring speed as shown in Table 20. The results of compositional analysis of the obtained α-olefin oligomers are shown along with shape of the by-product polymers and other data in Table 19.

Table 19(I)

	Example		
	62	63	64
Kind of solvent (amount:liter)	HP(1)	HP(1)	HP(1)
Reaction temperature (°C)	40	60	60
Ethylene pressure Pa(Kg/cm^2)	34.3×10^5 (35)	34.3×10^5 (35)	34.3×10^5 (35)
Reaction time (hour)	1.0	1.0	1.0
Stirring speed (r.p.m.)	400	600	800
⟨Product yield (g/hour)⟩	102.7	102.7	102.5
⟨Compositional distribution (wt%)⟩			
C_4	15.3	15.8	15.5
C_6 (total)	74.2	73.9	74.5
1-hexene content in C_6 (wt%)	95.7	95.5	95.8
C_8	3.1	2.9	3.3
C_{10-20}	6.8	6.9	6.2
C_{22-30}	0	0	0

Table 19 (II)

	Example		
	62	63	64
Wax	0	0	0
Polyethylene (PE) (by-product)	0.61	0.50	0.50
⟨Shape of PE⟩	Granular	Granular	Granular
⟨Grain size of PE (μm)⟩	100~300	50~300	50~300
⟨Catalytic efficiency⟩	513	520	508
⟨Catalytic activity⟩	4936	5003	4888

Example 65

n-Heptane (4.90 litres), an n-heptane solution of pyrrole (6.22 mmol) and an n-heptane solution of triethylaluminium (40.00 mmol) were charged to a 10 litre autoclave which was the same as used in Example 1, while an n-heptane solution of chromium (III) 2-ethylhexanoate (1.00 g, 2.10 mmol) was charged to the catalyst feed pipe. The total amount of n-heptane was 5 litres.

First, the autoclave was heated to a temperature of 40°C and then ethylene was introduced thereinto from the catalyst feed pipe. The rupture plate was ruptured under ethylene pressure, introducing the chromium compound into the autoclave to start the oligomerization of ethylene. Ethylene was introduced until the overall pressure reached 35.28 x 10^5 Pa (35 kg/cm^2 (G)). Thereafter the overall pressure was kept at 35.28 x 10^5 Pa (35 kg/cm^2(G)), while maintaining the temperature at 40°C. One hour later, ethanol was injected into the autoclave to terminate the reaction. The resulting reaction mixture contained granular by-product polymers.

After releasing ethylene from the autoclave, the obtained reaction mixture was supplied into a vertical "Sharples Super Decanter" (manufactured by Tomoe Kogyo Co., Ltd.) to separate the by-product polymers. The separation was conducted at an external bowl speed of 4,000 r.p.m. and an internal screw speed of 3,500 r.p.m. The by-product polymers assumed a favorable fluid state like powder and could be efficiently separated from the reaction mixture. The results of gas chromatographic analysis of the obtained α-olefin oligomers are shown along with other data in Table 20.

Examples 66 and 67

The same procedure as in Example 65 was carried out except for a change of reaction temperature and solvent as shown in Table 20. The results of compositional analysis of the obtained α-olefin oligomers are shown along with other data in Table 20. In both Examples, granular polymers were formed as by-product polymers and these by-product polymers could be separated efficiently as in Example 65.

Table 20(I)

	Example		
	65	66	67
Kind of solvent (amount:liter)	HP(5)	HP(5)	HP(5)
Reaction temperature (°C)	40	60	60
Ethylene pressure Pa(Kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)	45.1 x 10^5 45
Reaction time (Hr)	1.0	1.0	1.0
⟨Product yield (g/hour)⟩	441	514	619

Table 20(II)

	Example		
	65	66	67
⟨Compositional distribution (wt%)⟩			
C_4	12.2	15.3	18.0
C_6 (total)	74.7	74.2	71.6
1-hexene content in C_6 (wt%)	96.2	95.7	96.0
C_8	2.1	3.1	3.2
$C_{10\text{-}20}$	20.0	6.8	6.7
$C_{22\text{-}30}$	0.1	0	0
Wax	0	0	0
Polyethylene (PE) (by-product)	0.7	0.6	0.4
⟨Shape of PE⟩	Granular	Granular	Granular
⟨Catalytic efficiency⟩	441	513	619
⟨Catalytic activity⟩	4239	4936	5952

Example 68

Octane (n-form: 90 % by weight; i-form: 10 % by weight) (980 ml), an octane solution of pyrrole (1.244 mmol) and an octane solution of triethylaluminium (8.000 mmol) were charged to a 2.4 litre autoclave which was the same as used in Example 1 while an octane solution of chromium (III) 2-ethylhexanoate (200 mg, 0.420 mmol) was charged to the catalyst feed pipe. The total amount of octane was 1 litre.

First, the autoclave was heated to a temperature of 60°C and then ethylene was introduced thereinto from the catalyst feed pipe at a temperature of 60°C. The rupture plate was ruptured under ethylene pressure, introducing the chromium compound into the autoclave to start the oligomerization of ethylene. Ethylene was introduced until the overall pressure reached 35.28 x 10^5 Pa (35 kg/cm^2(G)). Thereafter the overall pressure was kept at 35.28 x 10^5 Pa (35 kg/cm^2(G)), while maintaining the temperature at 60°C. One hour later, ethanol was injected into the autoclave to terminate the reaction. After releasing ethylene from the autoclave the by-product polymers (mostly polyethylene) in the reaction mixture were separated by filtration to recover the reaction mixture. The results of gas chromatographic analysis of the α-olefin oligomers in the reaction mixture are shown along with other data in Table 21 (Example 69A).

Then the reaction mixture was distilled and separated into an octane fraction, a fraction with 4-6 carbon atoms and a fraction with not less than 8 carbon atoms. The latter fraction was subjected to a hydrogenation treatment. This hydrogenation treatment was carried out at a temperature of 90°C under a pressure of 40.18 x 10^5 Pa (40 kg/cm^2(G)) by using a Pt/γ-alumina catalyst. The results of gas chromatographic analysis of the hydrogenation product are shown along with other data in Table 21 (Example 68A).

Then said octane fraction and the hydrogenation product were recycled to the oligomerization reaction system as a solvent and the same reaction as described above was repeated. The solvent composition in this reaction was total octane/$C_{10\text{-}20}$ = 98.9/1.1 (by weight). The results of gas chromatographic analyses of the α-olefin oligomers in the reaction mixture and said hydrogenation product are shown along with other data in Table 21 (Example 69B).

In Table 21, "OCT" denotes octane.

Table 21(I)

	Example	
	68A	68B
Kind of solvent (amount:l)	OCT(1)	OCT/C_{10-20}(98.9/1.1)(1)
Reaction temperature (°C)	60	60
Ethylene pressure Pa(Kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0
⟨Product yield (g/Hr)⟩	107.9	105.1
⟨Compositional distribution (wt%)⟩		
C_4	13.7	12.0
C_6 (total)	75.7	75.5
1-hexene content in C_6 (wt%)	95.9	95.5
C_8	2.9	3.8
C_{10-20}	7.3	8.3
C_{22-30}	0	0
Wax	0	0

Table 21(II)

	Example	
	68A	68B
⟨Compositional distribution of hydrogenated fraction⟩		
C_8	28.0	-
C_{10-20}	72.0	-
Polyethylene (PE) (by-product)	0.4	0.4
⟨Catalytic efficiency⟩	540	536
⟨Catalytic activity⟩	5189	5151

Example 69

In Example 59, after the by-product polymers (mostly polyethylene) in the reaction mixture had been separated from the reaction mixture, the filtrate was introduced into a 2-litre vessel equipped a condenser and stirrer, and extracted with a 10 % HNO_3 aqueous solution (organic layer/aqueous layer = 1/1 (v/v)) at a temperature of 50°C for one hour with stirring. Thereafter, the stirring was stopped and the solution was left still. Concentration of the metallic substances in the separated aqueous layer was determined by high-frequency plasma emission spectroscopic analysis. As a result, chromium and alumina were detected, and their amount as determined from the calculation of concentration was substantially same as the amount used as catalyst components in the reaction.

Example 70

The same procedure as in Example 69 was conducted except that 20% NaOH aqueous solution was used instead of 10% HNO_3 aqueous solution. Chrominum and aluminium were recovered in NaOH aqueous solution, quantitatively.

Example 71

1-Hexene (980 ml), an n-heptane solution of pyrrole (1.244 mmol) and an n-heptane solution of triethylaluminium (8.000 mmol) were charged to a 2.4 litre autoclave which was the same as used in Example 1 while a heptane solution of chromium (III) 2-ethylhexanoate (200 mg, 0.420 mmol) was charged to the catalyst feed pipe. The total amount of 1-hexene and n-heptane was 1 litre.

First, the autoclave was heated to a temperature of 60°C and then ethylene was introduced thereinto from the catalyst feed pipe at a temperature of 60°C. The rupture plate was ruptured under ethylene pressure to introduce the chromium compound into the autoclave to start the oligomerization of ethylene. Ethylene was introduced until the overall pressure reached 35.28 x 10^5 Pa (35 kg/cm^2(G)). Thereafter the overall pressure was kept at 35.28 x 10^5 Pa (35 kg/cm^2(G)), while maintaining the temperature at 60°C. One hour later, ethanol was injected into the autoclave to terminate the recction.

After releasing ethylene from the autoclave, the by-product polymers (mostly polyethylene) in the reaction mixture were separated by filtration to obtain α-olefin oligomers. The results of gas chromatographic analysis of the obtained α-olefin oligomers are shown along with other data in Table 22.

In Table 22, "HEX" denotes 1-hexene and "OCTE" denotes 1-octene. The Amount is the combined amount of α-olefin and solvent.

Example 72

The same procedure as in Example 71 was conducted except that 1-octene (980 ml) was used in place of 1-hexene (980 ml). The results are shown in Table 22.

Table 22(I)

	Example	
	71	72
Kind of α-olefin (amount:l)	HEX(1)	OCTE(1)
Reaction temperature (°C)	60	60
Ethylene pressure Pa(Kg/cm^2(G))	35.28 x 10^5 (35)	35.28 x 10^5 (35)
Reaction time (Hr)	1.0	1.0
⟨Product yield (g/hour)⟩	75.2	111.4

Table 22(II)

	Example	
	71	72
⟨Compositional distribution (wt%)⟩		
C_{10}	29.2	4.3
C_{12}	0.8	22.7
C_4	18.4	13.7
C_6	43.2	46.9
C_8	5.3	9.2
$C_{14\text{-}20}$	2.7	2.6
$C_{22\text{-}30}$	0	0.1
Wax	0	0
Polyethylene (PE) (by-product)	0.4	0.6
⟨Catalytic efficiency⟩	376	557
⟨Catalytic activity⟩	3613	5355

Claims

1. A process for preparing an α-olefin oligomer which comprises oligomerizing an α-olefin in a solvent in the presence of a chromium-based catalyst system comprising a combination of at least a chromium compound; ammonia, an amine or metal amide; and an alkylaluminium compound, in a contacting mode that the chromium compound and the alkylaluminium compound are not previously contacted with each other.

2. A process according to claim 1 wherein the α-olefin and the chromium compound are introduced into a solution comprising the ammonia, amine or metal amide and the alkylaluminium compound.

3. A process according to claim 1 wherein the α-olefin and the alkylaluminium are introduced into a solution comprising the chromium compound and the ammonia, amine or metal amide.

4. A process according to claim 1 wherein the α-olefin, the ammonia, amine or metal amide, and the alkylaluminium compound are introduced into a solution comprising the chromium compound.

5. A process according to claim 1 wherein the α-olefin, the chromium compound and the ammonia, amine or metal amide are introduced into a solution comprising the alkylaluminium compound.

6. A process according to claim 1 wherein the chromium compound, the ammonia, amine or metal amide, the alkylaluminium compound and the α-olefin are introduced into a reactor simultaneously and separately.

7. A process according to any one of the preceding claims wherein the molar ratio of (a) the chromium compound, (b) the ammonia, amine or metal amide, and (c) the alkylaluminium compound is (a) : (b) : (c) = 1: 2 to 4: 4 to 8, and the reaction is carried out at a temperature of 25 to 70°C.

8. A process according to any one of the preceding claims wherein the reaction is carried out in the presence of a non-coordinating Lewis acid-containing compound.

9. A process according to claim 8 wherein the α-olefin and the chromium compound are introduced into a solution comprising the ammonia, amine or metal amide, the alkylaluminium compound and the non-coordinating Lewis acid-containing compound.

10. A process according to claim 8 wherein the α-olefin, the chromium compound and the ammonia, amine or metal amide are introduced into a solution comprising the alkylaluminium compound and the non-coordinating Lewis acid-containing compound.

11. A process according to claim 8 wherein the α-olefin and the alkylaluminium compound are introduced into a solution comprising the chromium compound, the ammonia, amine or metal amide and the non-coordinating Lewis acid-containing compound.

12. A process according to any one of the preceding claims wherein the reaction is carried out in the presence of a non-conjugated diene compound.

13. A process according to any one of the preceding claims wherein the reaction is carried out in the presence of an aromatic hydrocarbon compound.

14. A process according to any one of the preceding claims wherein the oligomerization is carried out in a saturated hydrocarbon solvent having not more than 7 carbon atoms at a temperature of 25 to 70°C, and then by-product polymers in the reaction mixture are separated and removed to recover the α-olefin oligomer without melting the by-product polymers.

15. A process according to any one of the preceding claims wherein the reaction mixture comprising the catalyst components is contacted with an acidic or alkaline aqueous solution to remove the catalyst components.

16. A process according to any one of the preceding claims for producing 1-hexene which comprises carrying out oligomerization of ethylene in a reaction solvent having a higher boiling point than that of 1-hexene under a pressure of not less than 107.8 x 10^4 Pa (10 kg/cm^2(G)) to obtain an α-olefin oligomer composition comprising 1-hexene, then reducing the pressure of the reaction system to not more than 3.92 x 10^5 Pa (3 kg/cm^2(G)) by degassing, and separating the by-products therefrom.

17. A process according to any one of the preceding claims for producing 1-hexene wherein an oligomerization reaction of ethylene is carried out to obtain an α-olefin oligomer composition with a 1-hexene content of not less than 50 wt%, then 1-hexene and the reaction solvent are distilled off from the reaction mixture and the recovered reaction solvent is recycled to the reaction system.

Patentansprüche

1. Verfahren zur Herstellung eines α-Olefin-Oligomeren, umfassend Oligomerisierung eines α-Olefins in einem Lösungsmittel in Gegenwart eines Katalysatorsystems auf Chrombasis, das eine Kombination aus mindestens einer Chromverbindung, Ammoniak, einem Amin oder Metallamid und einer Alkylaluminiumverbindung umfaßt, in einer solchen Kontaktierungsweise, daß die Chromverbindung und die Alkylaluminiumverbindung vorher miteinander nicht in Kontakt kommen.

2. Verfahren nach Anspruch 1, dadurch **gekennzeichnet,** daß man das α-Olefin und die Chromverbindung in eine Lösung einführt, die das Ammoniak, das Amin oder das Metallamid und die Alkylaluminiumverbindung umfaßt.

3. Verfahren nach Anspruch 1, dadurch **gekennzeichnet,** daß man das α-Olefin und die Alkylaluminiumverbindung in eine Lösung einführt, die die Chromverbindung und das Ammoniak, das Amin oder das Metallamid umfaßt.

4. Verfahren nach Anspruch 1, dadurch **gekennzeichnet,** daß man das α-Olefin, das Ammoniak, das Amin oder das Metallamid und die Alkylaluminiumverbindung in eine Lösung einführt, die die Chromverbindung enthält.

5. Verfahren nach Anspruch 1, dadurch **gekennzeichnet,** daß man das α-Olefin, die Chromverbindung und das Ammoniak, das Amin oder das Metallamid in eine Lösung einführt, die die Alkylaluminiumverbindung enthält.

6. Verfahren nach Anspruch 1, dadurch **gekennzeichnet,** daß man die Chromverbindung, das Ammoniak, das Amin oder das Metallamid, die Alkylaluminiumverbindung und das α-Olefin gleichzeitig und getrennt in einen Reaktor einführt.

7. Verfahren nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet,** daß das Molverhältnis von (a) Chromverbindung, (b) Ammoniak, Amin oder Metallamid und (c) Alkylaluminiumverbindung (a) : (b) : (c) = 1 : 2 bis

4 : 4 bis 8 beträgt und daß man die Reaktion bei einer Temperatur von 25 bis 70°C durchführt.

8. Verfahren nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet,** daß man die Reaktion in Gegenwart einer eine nichtkoordinierende Lewis-Säure enthaltenden Verbindung durchführt.

9. Verfahren nach Anspruch 8, dadurch **gekennzeichnet,** daß man das α-Olefin und die Chromverbindung in eine Lösung einführt, die das Ammoniak, das Amin oder das Metallamid, die Alkylaluminiumverbindung und die eine nichtkoordinierende Lewis-Säure enthaltende Verbindung enthält.

10. Verfahren nach Anspruch 8, dadurch **gekennzeichnet,** daß man das α-Olefin, die Chromverbindung und das Ammoniak, das Amin oder das Metallamid in eine Lösung einführt, die die Alkylaluminiumverbindung und die eine nichtkoordinierende Lewis-Säure enthaltende Verbindung enthält.

11. Verfahren nach Anspruch 8, dadurch **gekennzeichnet,** daß man das α-Olefin und die Alkylaluminiumverbindung in eine Lösung einführt, die die Chromverbindung, das Ammoniak, das Amin oder das Metallamid und die eine nichtkoordinierende Lewis-Säure enthaltende Verbindung enthält.

12. Verfahren nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet,** daß man die Reaktion in Gegenwart einer nichtkonjugierten Dienverbindung durchführt.

13. Verfahren nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet,** daß man die Reaktion in Gegenwart einer aromatischen Kohlenwasserstoffverbindung durchführt.

14. Verfahren nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet,** daß man die Oligomerisierung in einem gesättigten Kohlenwasserstoff-Lösungsmittel mit nicht mehr als 7 Kohlenstoffatomen bei einer Temperatur von 25 bis 70°C durchführt und daß man sodann Nebenprodukt-Polymere in dem Reaktionsgemisch abtrennt und entfernt, um das α-Olefin-Oligomere zu gewinnen, ohne daß die Nebenprodukt-Polymere geschmolzen werden.

15. Verfahren nach einem der vorstehenden Ansprüche, dadurch **gekennzeichnet,** daß man das Reaktionsgemisch, das die Katalysatorkomponenten enthält, mit einer sauren oder alkalischen wäßrigen Lösung kontaktiert, um die Katalysatorkomponenten zu entfernen.

16. Verfahren nach einem der vorstehenden Ansprüche zur Herstellung von 1-Hexen, dadurch **gekennzeichnet,** daß man die Oligomerisierung von Ethylen in einem Reaktionslösungsmittel mit einem höheren Siedepunkt als derjenige von 1-Hexen unter einem Druck von nicht weniger als $107{,}8 \times 10^4$ Pa (10 kg/cm^2 (G)) zum Erhalt einer α-Olefin-Oligomer-Zusammensetzung, die 1-Hexen umfaßt, durchführt, daß man sodann den Druck des Reaktionssystems auf nicht mehr als $3{,}92 \times 10^5$ Pa (3 kg/cm^2 (G)) durch Entgasen vermindert und daß man die Nebenprodukte davon abtrennt.

17. Verfahren nach einem der vorstehenden Ansprüche zur Herstellung von 1-Hexen, dadurch **gekennzeichnet,** daß man eine Oligomerisierungsreaktion von Ethylen durchführt, um eine α-Olefin-Oligomer-Zusammensetzung mit einem 1-Hexengehalt von nicht weniger als 50 Gew.-% zu erhalten, daß man anschließend 1-Hexen und das Reaktionslösungsmittel von dem Reaktionsgemisch abdestilliert und daß man das wiedergewonnene Reaktionslösungsmittel in das Reaktionssystem zurückführt.

Revendications

1. Procédé pour préparer un oligomère d'α-oléfine, qui comprend l'oligomérisation d'une α-oléfine dans un solvant en présence d'un système catalytique à base de chrome, comprenant une combinaison d'au moins un composé du chrome ; l'ammoniac, une amine ou un amidure métallique ; et un composé alkylaluminium, dans un mode de contact tel que le composé du chrome et le composé alkylaluminium ne soient pas auparavant mis en contact mutuel.

2. Procédé selon la revendication 1, où l'α-oléfine et le composé du chrome sont introduits dans une solution comprenant l'ammoniac, l'amine ou l'amidure métallique, et le composé alkylaluminium.

3. Procédé selon la revendication 1, où l'α-oléfine et l'alkylaluminium sont introduits dans une solution comprenant le composé du chrome et l'ammoniac, l'amide ou l'amidure métallique.

4. Procédé selon la revendication 1, où l'α-oléfine, l'ammoniac, l'amine ou l'amidure métallique, et le composé alkyla-

luminium sont introduits dans une solution comprenant le composé du chrome.

5. Procédé selon la revendication 1, où l'α-oléfine, le composé du chrome et l'ammoniac, l'amine ou l'amidure métallique sont introduits dans une solution comprenant le composé alkylaluminium.

6. Procédé selon la revendication 1, où le composé du chrome, l'ammoniac, l'amine ou l'amidure métallique, le composé alkylaluminium et l'α-oléfine sont introduits dans un reacteur simultanément et séparément.

7. Procédé selon l'une quelconque des revendications précédentes, où le rapport molaire de (a) le composé du chrome, (b) l'ammoniac, l'amine ou l'amidure métallique, et (c) le composé alkylaluminium est (a)/(b)/(c) = 1/2 à 4/4 à 8, et la réaction est effectuée à une température de 25 à 70°C.

8. Procédé selon l'une quelconque des revendications précédentes, où la réaction est effectuée en présence d'un composé contenant un acide de Lewis non coordinant.

9. Procédé selon la revendication 8, où l'α-oléfine et le composé du chrome sont introduits dans une solution comprenant l'ammoniac, l'amine ou l'amidure métallique, le composé alkylaluminium et le composé contenant un acide de Lewis non coordinant.

10. Procédé selon la revendication 8, où l'α-oléfine, le composé du chrome et l'ammoniac, l'amine ou l'amidure métallique sont introduits dans une solution comprenant le composé alkylaluminium et le composé contenant un acide de Lewis non coordinant.

11. Procédé selon la revendication 8, où l'α-oléfine et le composé alkylaluminium sont introduits dans une solution comprenant le composé du chrome, l'ammoniac, l'amine ou l'amidure métallique et le composé contenant un acide de Lewis non coordinant.

12. Procédé selon l'une quelconque des revendications précédentes, où la réaction est effectuée en présence d'un diène non conjugué.

13. Procédé selon l'une quelconque des revendications précédentes, où la réaction est effectuée en présence d'un hydrocarbure aromatique.

14. Procédé selon l'une quelconque des revendications précédentes, où l'oligomérisation est effectuée dans un solvant hydrocarboné saturé n'ayant pas plus de 7 atomes de carbone, à une température de 25 à 70°C, puis les polymères constituant des sous-produits dans le mélange réactionnel sont séparés et éliminés pour récupérer l'oligomère d'α-oléfine sans fusion des polymères constituant les sous-produits.

15. Procédé selon l'une quelconque des revendications précédentes, où le mélange réactionnel comprenant les composants catalytiques est mis en contact d'une solution aqueuse acide ou alcaline pour éliminer les composants catalytiques.

16. Procédé selon l'une quelconque des revendications précédentes pour la production de 1-hexène, qui comprend la réalisation de l'oligomérisation de l'éthylène dans un solvant réactionnel ayant un point d'ébullition supérieur à celui du 1-hexène, sous une pression d'au moins 107,8 x 10^4 Pa (10 kg/cm^2 (manométriques)), pour obtenir une composition d'oligomères d'α-oléfine comprenant du 1-hexène, puis l'abaissement de la pression du système réactionnel à une valeur ne dépassant pas 3,92 × 10^5 Pa (3 kg/cm^2 (manométriques)) par dégazage et la séparation des sous-produits de celui-ci.

17. Procédé selon l'une quelconque des revendications précédentes pour la production de 1-hexène, où l'on effectue une réaction d'oligomérisation de l'éthylène pour obtenir une composition d'oligomères d'α-oléfine ayant une teneur en 1-hexène d'au moins 50 % en poids, puis le 1-hexène et le solvant réactionnel sont éliminés par distillation du mélange réactionnel et le solvant réactionnel récupéré est recyclé dans le système réactionnel.